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INTERNATIONAL ATOMIC WEIGHTS

1948

PUBLISHED BY THE *Journal of the American Chemical Society*

Element	*Symbol*	*Atomic number*	*Atomic weight*	*Element*	*Symbol*	*Atomic number*	*Atomic weight*
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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Thomas Midgley, Jr. 1889–1944)
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After graduation from college, Dr. Midgley went directly into an industry typical of the fields into which the users of this book may go. He was trained as a mechanical engineer but soon found himself involved in chemistry, a complication which may meet any young man in this age. Without further formal training, he made himself one of the outstanding chemists of the world. Besides inventing ethyl gasoline, he was mainly responsible for Freon, the best of modern refrigerants. He also did outstanding work in the problems of natural and synthetic rubber. He was president of the American Chemical Society, whose 59,000 members constitute the world's largest scientific society. For many years, he was also chairman of its board of directors. To him came practically all the coveted medals of chemistry—the Nichols, the Perkin, the Priestley, the Willard Gibbs, and the Longstreth. With all his scientific work he was a prince of good fellows and a bit of an amateur poet.

F. C. Whitmore

General and Applied Chemistry

A BRIEF COLLEGE COURSE

by ARNOLD J. CURRIER
Professor of Chemistry
The Pennsylvania State College

and ARTHUR ROSE
Associate Professor of Chemical Engineering
The Pennsylvania State College

FIRST EDITION
THIRD IMPRESSION

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PREFACE

This textbook is designed for students in applied science and technology, who normally take a brief, one-year college course in general chemistry. About ten years ago, the authors felt the need of a book that would adequately present such a brief course. To meet this need, they prepared a mimeographed booklet, "Notes for Chemistry 3 and 4," and used it for several years in their classes. In expanded form, these notes are now presented as a textbook.

In preparing a textbook in chemistry for students in agriculture, engineering, home economics, and other applied sciences, the objective should be clearly defined. Obviously, few of these students expect to follow chemistry as a profession. Chemistry is, therefore, not to be their major field, but it is to serve as a basis for understanding the nature of the materials with which they are to work and the environment in which they live. To provide this basis, both the "pure science" of chemistry and the applications are presented. Sections on fuels, foods, fertilizers, explosives, plastics, etc., may be assigned according to the special interests or needs of the class. A few of the longer chapters, for example, IX and XXVIII, may be presented in two assignments. An effort has been made to correlate the practical applications of materials with their fundamental properties.

It is the conviction of the authors, that textbooks in general chemistry contain far more material than can be adequately taught in a one-year course. Too much material is likely to be confusing rather than helpful to the average student. The choice and arrangement of topics included in this book have been dictated largely by teaching experience. For example, the chapters pertaining to the metals appear approximately in the order in which the metallic ions are studied in qualitative analysis. Some of the reactions of the metallic ions in qualitative analysis are included in the chapters relating to the metals and their compounds. In the authors' classes, about half of the laboratory work of the second semester is on qualitative analysis. Students have a special interest in this work and, from it, obtain a broader knowledge of inorganic chemistry.

The exercises are placed within, rather than at the end of, the chapters. This arrangement helps the student to see the relationship between the text material and the exercises. Courses in which this book is used should include a well-planned series of class or lecture demonstrations and experiments to be performed individually by the student in the laboratory.

Authors, publishers, and industrial concerns have kindly furnished data and illustrative material. Appreciation is expressed also to Profs. G. C. Chandlee and J. H. Olewine, Department of Chemistry; R. C. Raymond, Department of Physics; F. G. Merkle, Department of Agronomy, of The Pennsylvania State College; Dr. C. H. Jeglum, Philadelphia Quartz Company, and Dr. E. M. Symmes, Hercules Powder Company. These individuals kindly read the chapters relating to their special fields of chemistry and offered helpful criticisms. Acknowledgments for their suggestions are due also to the authors' colleagues, Profs. H. H. Appledorn, G. E. Cohen, A. H. Holtzinger, and L. R. Parks, who teach general chemistry, and to Arnold J. Currier, Jr., who carefully read the manuscript. The authors will gratefully receive corrections and suggestions that will enhance the usefulness of the book.

ARNOLD J. CURRIER
ARTHUR ROSE

STATE COLLEGE, PA.
March, 1948

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CHAPTER I

ELEMENTS AND COMPOUNDS

We live in a material world. Our existence depends upon the use of essential materials such as foods and fuels. The engineer, the farmer, the housewife, and the manufacturer all work with materials. Chemistry is the science that is concerned with the study of the composition and the properties of these materials. Some knowledge of chemistry, therefore, is desirable in a general education and is essential in certain technical fields, such as engineering, agriculture, and home economics. For the profession of chemistry and chemical engineering, several years of intensive training in chemistry are, of course, required.

1. Chemical Changes and Chemistry. *Changes involving the transformation of one or more kinds of matter into entirely different kinds are called chemical changes.* Chemistry is the study of these chemical changes and includes the study of methods for the purification, separation, classification, and description of all the various kinds of matter. The result of this study is, of course, very practical since it gives the power to control natural or known changes, as well as the ability to produce entirely new kinds of matter by chemical changes. Chemical changes are also used to separate, to purify, and to increase the supply of existing kinds of matter. Practically all the conveniences and comforts of civilized life depend upon the possibility of using chemical changes to make kinds of matter that do not naturally occur on or in the earth. Much of the world's food supply is produced with the aid of chemicals that stimulate growth or deter insect activities. In many cases foods are preserved (in cans or out) by chemicals or chemical processes. Cooking and digestion are essentially chemical in nature. A large proportion of the clothing of today is made by processes entirely chemical in nature, while other textiles are treated with chemicals to clean, bleach, and dye them. The concrete, steel, glass, plaster, and mortar, the roofing, and even the wood of modern houses are in many cases made by chemical processes or treated with chemicals during manufacture. The supplies of fuels and lubricants essential for transportation by automobile, train, airplane, and ship are increasingly dependent upon chemical changes.

Exercises

1. Name five kinds of matter which are well known or much used but which do not occur naturally anywhere on earth.
2. Name five important chemical industries.

2. Chemical Changes. If a strip of the metal magnesium is held by means of forceps in a bunsen burner flame, the metal burns rapidly, gives off a very brilliant light, and is converted to a white ashlike residue. (The eyes should be turned away from the light.) In the process of burning, the magnesium combines with the oxygen of the air, forming magnesium oxide. The chemical change may be stated in a "word equation" as follows:

$$\underset{\text{metal}}{\text{Magnesium}} + \underset{\text{nonmetal}}{\text{oxygen}} \text{ forms } \underset{\text{metallic oxide}}{\text{magnesium oxide}}$$

Another interesting illustration is the combination (reaction) of powdered iron with powdered sulfur. About 5.5 g. of powdered iron is thoroughly mixed with about 3.2 g. powdered sulfur in a test tube. Slightly heating the test tube near the top or bottom of the mixture is sufficient to start the reaction, which is evident by the red glow emitted. The brittle, dark gray product called *ferrous sulfide* can be examined by breaking the test tube after it has cooled. The chemical change or reaction can be expressed by a word equation as follows:

$$\underset{\text{metal}}{\text{Iron}} + \underset{\text{nonmetal}}{\text{sulfur}} \text{ forms } \underset{\text{a sulfide}}{\text{ferrous sulfide}}$$

The weights, 5.5 g. iron and 3.2 g. sulfur, are the reacting weights based upon the atomic weights discussed in Sec. 7.

The burning of fuels, the corrosion of metals, the combustion of gasoline in a motor, the processes of photosynthesis, digestion, and fermentation, the rusting of iron, the souring of milk, the action of baking powder, the action on a photographic film during exposure, developing, and printing are all examples of chemical changes. In a chemical change, there is a change in the composition or identity of the substance used.

3. Physical Changes. A piece of platinum wire held in a bunsen burner flame appears to glow brightly. In contrast with copper or magnesium, however, it is not changed in the heating process. When cooled, the platinum is found to have retained its original appearance. Another more familiar illustration is the conversion of ice to water and then to steam by application of heat, or the reverse process, the conversion of steam to water and to ice by removal of heat. These *physical changes* may be indicated as follows:

Add heat

$$\underset{\text{solid}}{\text{Ice}} \rightleftarrows \underset{\text{liquid}}{\text{water}} \rightleftarrows \underset{\text{gas}}{\text{steam}}$$

Remove heat

Although the physical state is changed from ice to water and then to steam (or vice versa), there is no change in the composition or chemical identity of the water. In other words, we may have water in the solid, the liquid, or the gaseous state.

Chemical changes may be distinguished from physical changes. In physical changes, no new or different kind of matter is produced. Examples of physical changes are the melting of a solid, the change of a liquid into its vapor (evaporation or boiling), and all other changes of state, as well as the processes of dissolving, pulverizing, crystallizing, distilling, and extracting. Chemical changes and physical changes often occur together, and of course there are some changes that are difficult to classify as either chemical or physical.

4. Substances, Mixtures, Elements, Compounds. Most materials found in nature or produced by chemical processes are mixtures of two or more substances. For example, concrete is a mixture of cement and stone. *A substance is a particular kind of matter*, such as salt, sugar, sulfur, or iron. A method can usually be found to separate the substances in a mixture, and thus it becomes possible to study each one separately in its pure state. Chemists have purified, studied, named, and described more or less completely about 300,000 different kinds of substances. The results are recorded in chemical journals and reference books. Practically all of this work has been done during the past 200 years and, of course, is still being continued. Very early during this work, as the number of substances purified became larger and larger, it became evident that many of them could be (1) *changed (decomposed) into two or more other substances* or (2) *made (synthesized) by combining two or more other substances.*

Substances possessing either or both of these characteristics were called *compound substances*, or *chemical compounds*, or, simply, *compounds.* There were, however, a very few substances (only a few dozen at first) that did not possess either of the above characteristics. These simple substances, or *elements*, could be neither decomposed into, nor made by combination of, other substances. Iron and sulfur are examples of well-known elements; salt and sugar are examples of compounds.

It is important to note that the above discussion is expressed in the past tense because during the present century methods have been discovered for decomposing and synthesizing elements. *An element may be defined as a substance that can be neither decomposed nor made by combination from other substances by ordinary chemical methods.* Even at the present time, elements cannot be decomposed or synthesized except by certain very special types of recently developed transmutation processes. These processes have been used on a large scale in the production of the atomic bomb. Transmutation processes involve changes within the interior parts or nuclei of the atoms of the elements concerned, while ordinary chemical changes involve only changes in the exterior parts of atoms.

5. Atoms, Molecules, and Atomic Theory. The idea that all matter is composed of extremely small indivisible particles or atoms is very old. Greek and even earlier philosophers developed this idea to a limited extent, but in no case was there any attempt to present experiments supporting their ideas or theories. The modern atomic theory has developed from the atomic theory of John Dalton, first stated by him shortly after 1800. The essential points, revised in accordance with modern discoveries, are given in the following section.

6. The Modern Atomic Theory. *Atoms.* All substances are composed of very small particles called *atoms.*

Atoms and Elements. All the atoms of each element are almost exactly alike, while the atoms of different elements are distinctly different. (Atoms of a given element may vary in weight.)

Molecules of an Element. Atoms of the same element may unite with one another to form molecules of the element. A sample of the element oxygen (oxygen gas) is composed of oxygen atoms joined in pairs to form oxygen, O_2, molecules. Some gases, *e.g.*, helium, He, contain only 1 atom in the molecule.

Molecules of Compounds. Atoms of different elements may unite with one another to form a molecule of some compound. A molecule may contain 2, 3, or more atoms, but for any given compound the number of atoms in the molecule is always the same; for example, carbon dioxide, CO_2, contains 3 atoms.

Molecules and Chemical Change. Chemical changes consist of the reaction of molecules or uncombined atoms of various kinds with one another to form molecules or uncombined atoms different from those originally present. Heat, light, electricity, or other forms of energy may or may not be necessary to start and maintain such changes.

7. Elements, Symbols, and Atomic Weights. A few of the most common chemical elements are oxygen, nitrogen, hydrogen, carbon, sulfur, iron, and copper. Each element has a characteristic symbol, such as H for hydrogen, O for oxygen, C for carbon, which is used not only as an abbreviation for the name of the element but also in chemical calculations to represent a *definite weight* of the element. To each element there is assigned an *atomic weight*, which is the *relative weight of its atom compared with the weight of the oxygen atom* (16). A full discussion of the method of obtaining these weights and their meaning and significance would require much of our time and is relatively unimportant at this point. It is necessary, however, to be able to use them. Atomic weights are not to be memorized but are obtained by reference to a table (see inside front cover).

Exercise

3. (*a*) Using the table at the front of this book, find the symbols and atomic weights of 10 common elements. (*b*) How many elements are listed in the table?

For purposes of calculation, the symbol H represents 1.008 parts by weight of hydrogen; O, 16 parts by weight of oxygen; C, 12 parts by weight of carbon; 2C, twice 12 or 24 parts by weight of carbon; and O_2, twice 16 or 32 parts by weight of oxygen. The unit of weight generally used is the gram. Any unit of weight, however, can be employed, provided it is used consistently throughout a given calculation. In elementary chemistry courses, it is customary to neglect the fractions given in the atomic weight table and use the nearest whole number.

8. Compounds and Chemical Formulas. A few common chemical compounds are water, sulfuric acid, sugar, and salt. Every chemical compound may be represented by a chemical formula; *e.g.*, H_2O for water, H_2SO_4 for sulfuric acid, NaCl for common salt (sodium chloride), $C_{12}H_{22}O_{11}$ for sugar. The formula not only is used as an abbreviation for the name of the compound, but represents a definite weight of the compound—the *formula weight*—or the so-called *molecular weight*.

9. Formula Weights, Molecular Weights, the Mole. Formula weights are obtained from formulas by adding the atomic weights represented by a formula. Thus, the formula weight of water, H_2O, is 18. There are represented two atomic weights of H and one atomic weight of O. The formula weight of

H_2SO_4 is 98; of NaCl, 58; of sugar, 342. Each one of the formula weights (molecular weights) is called a *mole.* Thus, 18 g. H_2O is 1 gram mole of water; 18 lb. H_2O is 1 pound mole.

The formula of slaked lime or calcium hydroxide is $Ca(OH)_2$. There are represented one atomic weight of calcium, two atomic weights of oxygen, and two atomic weights of hydrogen. The formula weight is 74. The numerical statement for the calculation of the formula weight of $Ca(OH)_2$ can be shown as follows:

Ca.................................... $40 \times 1 = 40$
O..................................... $16 \times 2 = 32$
H..................................... $1 \times 2 = \underline{2}$
Formula weight $= 74$

Exercises

4. Calculate the formula weights of (*a*) carbon dioxide, CO_2; (*b*) water, H_2O; (*c*) copper sulfate, $CuSO_4$; (*d*) calcium carbonate, $CaCO_3$.

5. Calculate the formula weights of (*a*) oxygen, O_2; (*b*) sodium hydroxide, NaOH; (*c*) sodium peroxide, Na_2O_2; (*d*) glycerin, $C_3H_5(OH)_3$.

6. Calculate the number of gram moles of each of the following: (*a*) 320 g. O_2; (*b*) 4 g. NaOH; (*c*) 7.8 g. Na_2O_2; (*d*) 1800 g. H_2O; (*e*) 8.8 g. CO_2.

10. Calculation of Percentage Composition from Formulas.

The formula NaCl represents one formula weight of salt (58 parts by weight) formed by the union of one atomic weight of sodium (23 parts by weight of sodium) with one atomic weight of chlorine (35 parts by weight of chlorine). From this, it follows that

$$\frac{\text{At. wt. of sodium}}{\text{Formula weight of sodium chloride}} \times 100 = \frac{23}{58} \times 100$$
$$= \%\text{ sodium in sodium chloride}$$

$$\frac{\text{At. wt. of chlorine}}{\text{Formula weight of sodium chloride}} \times 100 = \frac{35}{58} \times 100$$
$$= \%\text{ chlorine in sodium chloride}$$

The percentage of oxygen in calcium hydroxide, $Ca(OH)_2$, may be calculated as follows:

$$\frac{16 \times 2}{74} \times 100 = \%\text{ oxygen in calcium hydroxide}$$

Exercises

7. Show how to calculate the percentage composition of (percentage of each element in) (*a*) HgO; (*b*) NaOH; (*c*) Na_2O_2; (*d*) CO_2; (*e*) H_2CO_3.

8. Show how to calculate the percentage composition of (*a*) $CuSO_4$; (*b*) $Al(OH)_3$; (*c*) C_2H_5OH; (*d*) $C_{12}H_{22}O_{11}$.

11. The Metric System. The following units of the metric system with the English equivalents are commonly used in scientific work and should be memorized:

1 kilogram = 1,000 grams (g.) = 2.2 pounds
1 gram = 1,000 milligrams (mg.)
1 liter = 1,000 milliliters (ml.) = 1.057 quarts
= 1,000 cubic centimeters (cc.) (approximately)
1 meter = 100 centimeters = 39.37 inches
= 1,000 millimeters (mm.)

Exercises

9. Convert 250 g. to (*a*) milligrams, (*b*) kilograms.
10. How many kilograms are there (*a*) in 220 lb., (*b*) in 10 lb.?
11. 2,500 ml. is equal to (*a*) how many liters, (*b*) how many quarts?
12. The height of the mercury column in a barometer is 760 mm. at sea level. This is equivalent to (*a*) how many centimeters, (*b*) how many inches?

SUGGESTED READING

The reading of selected articles in the chemical literature will be found very interesting and instructive. References are listed at the end of most of the chapters. A librarian will help locate the articles listed. The abbreviation, *J. Chem. Education*, refers to the *Journal of Chemical Education; Ind. Eng. Chem.* refers to the periodical, *Industrial and Engineering Chemistry.* Bound volumes of these journals are found in college and university libraries and in the larger city libraries.

COWARD, The Early Years of the Atomic Theory as Illustrated by Dalton's Own Note Books and Lecture Diagrams, His Apparatus, *J. Chem. Education*, **4,** 22 (1927).

HALVORSON, Chemistry in the Service of Agriculture, *J. Chem. Education*, **15,** 578 (1938).

CHAPTER II

FORMULAS AND EQUATIONS COMBINING PROPORTIONS BY WEIGHT

Having considered briefly the formulas of certain compounds, we are naturally interested in knowing how chemical formulas are obtained and how they are used to express chemical changes. In this chapter, we are to study these questions by reference to a number of illustrations some of which are included in the laboratory work.

1. Methods of Obtaining Chemical Formulas. The number of atoms in the formula of a compound is determined by calculations based upon a chemical analysis giving the percentage of the reacting weights of each element in the compound.

Exercises

1. Magnesium oxide contains 60 per cent magnesium and 40 per cent oxygen. What is its formula?

First: Divide the weight or the percentage of each element in the compound by the atomic weight of this element.

$$\frac{\%\ \text{Mg}}{\text{At. wt. Mg}} = \frac{60}{24} = 2.5 \text{ at. wts. of Mg} \qquad \frac{2.5}{2.5} = 1$$

$$\frac{\%\ \text{O}}{\text{At. wt. O}} = \frac{40}{16} = 2.5 \text{ at. wts. of O} \qquad \frac{2.5}{2.5} = 1$$

Second: Compare the numbers obtained in the first step to find the relative number of atomic weights of each element. In this case there are just as many atomic weights of magnesium (2.5) as there are atomic weights of oxygen. The formula is MgO.

2. Ferric oxide contains 70 per cent Fe and 30 per cent O. What is its formula?

$$\frac{\%\ \text{Fe}}{\text{At. wt. Fe}} = \frac{70}{56} = 1.25 \qquad \frac{1.25}{1.25} = 1 \qquad 1 \times 2 = 2$$

$$\frac{\%\ \text{O}}{\text{At. wt. O}} = \frac{30}{16} = 1.87 \qquad \frac{1.87}{1.25} = 1.5 \qquad 1.5 \times 2 = 3$$

The formula is Fe_2O_3.

3. Derive the formula of an oxide of nitrogen containing 63.6 per cent nitrogen and 34.6 per cent oxygen.

4. Derive the formulas of the following compounds:
   (*a*) 42.85 per cent carbon, 57.15 per cent oxygen.
   (*b*) 27.1 per cent sodium, 16.4 per cent nitrogen, 56.5 per cent oxygen.

(c) 25.4 per cent sodium, 39.2 per cent chlorine, 35.4 per cent oxygen.
(d) 57.86 per cent platinum, 42.14 per cent chlorine.

5. For four different oxides of lead, the percentage compositions are given below. Derive the formula of each.

	1	2	3	4
Pb, %	92.8	86.6	89.65	90.65
O, %	7.2	13.3	10.35	9.35

2. Empirical Formulas and Molecular Formulas. It is to be observed that the above method gives only the relative number of atoms in the formula and not the total number. For instance, with reference to Exercise 1, the formulas Mg_2O_2 or Mg_3O_3 also represent equal numbers of atomic weights of Mg and O, and it might be that one of these formulas represents the actual composition of magnesium oxide. Thus, the method does not distinguish between the formulas, MgO, Mg_2O_2, Mg_3O_3, etc. In practice, the results of such a calculation are always expressed by the simplest possible formula, which is called the *empirical formula.* Additional experiments and calculations (molecular weight determinations)[1] are required to obtain the molecular formula that gives the total number as well as the relative number of atoms in the molecule. The molecular weight of a gas or a volatile liquid may be determined merely by finding the weight of 22.4 l. of the gas or vapor of the liquid at *standard conditions* (0°C. and 760 mm. pressure). The molecular weight of certain substances in solution may be determined by a study of the boiling point, freezing point, or vapor pressure. The molecular weights of solids and pure liquids may sometimes be determined by X ray or other special methods. In some cases, however, it has been impossible to determine molecular weights by any method. In such cases, there is no alternative but to use the empirical formula.

3. Molecules and Formulas of Compounds. Each different compound is composed of certain elements, and the chemical formula indicates the number and kind of atoms in the compound. Since each kind of atom has a characteristic weight (atomic weight), these weights taken together according to the number of atoms uniting to form the compound determine the definite composition of the compound.

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[1] For a further discussion of the determination of molecular weights, refer to Chap. XIII.

4. Law of Constant Composition. *A given chemical compound always contains the same elements in a definite proportion by weight.* The importance of this law should be quite obvious to the student from the preceding discussions and calculations. It is the foundation upon which all quantitative chemical relationships are based. If the law were not true, chemistry would not be an exact science as it is today. The introduction of the chemical balance by the French chemist Lavoisier laid the foundations for understanding the exact weight relationships in chemical reactions. The balance is still an indispensable tool in quantitative chemical work. For this reason, beginning students in general chemistry should, if possible, perform experiments involving the use of suitable inexpensive balances in order to gain a real appreciation and understanding of the weight relationships in chemical reactions.

5. Atoms, Molecules, and Equations. A chemical equation indicates the composition of the substances used and formed in a chemical reaction. From the equation one may calculate the relative weights of the various substances used and produced by the reaction. For example, when sodium peroxide, Na_2O_2, is placed in water, H_2O, two products, sodium hydroxide, NaOH, and oxygen, O_2, are formed. The equation, with the relative *reacting weights*, for this reaction is indicated as follows:

$$\begin{array}{ccccccc} \text{Sodium peroxide} & + & \text{water} & \text{forms} & \text{sodium hydroxide} & + & \text{oxygen} \\ 2Na_2O_2 & + & 2H_2O & \rightarrow & 4NaOH & + & O_2 \\ 2(78) & + & 2(18) & \rightarrow & 4(40) & + & 32 \\ 156 & + & 36 & \rightarrow & 160 & + & 32 \end{array}$$

The equation indicates (1) that 2 molecules of sodium peroxide (each containing 2 atoms of sodium and 2 atoms of oxygen) react with 2 molecules of water to form 4 molecules of sodium hydroxide and 1 molecule of oxygen, (2) that 156 parts by weight of sodium peroxide react with 36 parts by weight of water to form 160 parts by weight of sodium hydroxide plus 32 parts by weight of oxygen.

The same equation could be written in a more complete form in order to show more readily the total number of molecules (and atoms) involved in the reaction:

$$\begin{array}{c} Na_2O_2 + H_2O \\ Na_2O_2 + H_2O \end{array} \rightarrow \begin{array}{c} NaOH \\ NaOH \\ NaOH \\ NaOH \end{array} + O_2$$

It is to be noted that the total number of atoms of sodium, oxygen, and hydrogen is the same on both sides of the equation, namely, 4 atoms of sodium, 6 atoms of oxygen, and 4 atoms of hydrogen. In other words, the equation is *balanced.* It must be kept in mind, however, that a chemical equation for a reaction must always be a true statement of the composition of all substances used and formed in the reaction. The reaction indicated above will be demonstrated in the study of oxygen.

6. Weight Relations in Chemical Reactions. Because each compound contains a definite proportion of each constituent element by weight, it is possible to calculate the weights of substances used and formed in a chemical reaction, provided the equation for the reaction is known. Consider, for example, the reaction of calcium oxide or quicklime with water forming calcium hydroxide or hydrated lime.[1] The equation with the formula weights for this reaction is as follows:

$$\underset{56}{CaO} + \underset{18}{H_2O} \rightarrow \underset{74}{Ca(OH)_2}$$

The formula weights that represent the relative combining or reacting weights may be expressed in any desired units, *e.g.*, in grams, pounds, or tons. The weight relationships may be expressed as follows: one formula weight of calcium oxide (56) reacts with one formula weight of water (18), forming one formula weight (74) of calcium hydroxide.

Exercises

6. Calculate (*a*) the weight in pounds of water required to react with 280 lb. calcium oxide, (*b*) the weight, in pounds, of calcium hydroxide that is formed. The problem is calculated as follows:

(*a*) 56 lb. CaO reacts with 18 lb. H_2O.
1 lb. CaO reacts with $^{18}/_{56}$ lb. H_2O.
280 lb. CaO reacts with $^{18}/_{56} \times 280 = 90$ lb. water.
(*b*) 56 lb. CaO forms 74 lb. $Ca(OH)_2$.
1 lb. CaO forms $^{74}/_{56}$ lb. $Ca(OH)_2$.
280 lb. CaO forms $^{74}/_{56} \times 280 = 370$ lb. $Ca(OH)_2$.

7. Calculate (*a*) the weight of calcium oxide, (*b*) the weight of water, required to make 1 ton (2,000 lb.) of calcium hydroxide (hydrated lime).

SUGGESTION: Begin with the following statement:

74 lb. $Ca(OH)_2$ requires 56 lb. CaO

8. Calculate (*a*) the weight of water that will react with 7.8 g. sodium peroxide, Na_2O_2, (*b*) the weight of sodium hydroxide that is formed.

9. Calculate (*a*) the weight of sodium peroxide required to produce 4 g. oxygen, (*b*) the weight of water required.

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[1] For a more detailed study of the manufacture of lime, refer to Chap. XXIX.

7. Law of Conservation of Mass. This law, made known by Lavoisier in 1785 and confirmed by other investigators, may be stated as follows: *In a chemical reaction, the total weight of the substances used is equal to the total weight of the substances formed.* Referring to the reaction of calcium oxide with water (II. 6), 56 lb. calcium oxide plus 18 lb. water equals the weight of calcium hydroxide formed (74 lb).

Exercises

10. Illustrate the law of conservation of mass with reference to the reaction of sodium peroxide, Na_2O_2, with water, H_2O, forming sodium hydroxide, NaOH, and oxygen, O_2.

11. (*a*) Account for the loss in weight of coal when it is burned. (*b*) Does the law of conservation of mass apply in this case?

12. 10 g. iron and 10 g. sulfur are mixed together and heated, forming ferrous sulfide. Calculate (*a*) which element is present in excess, (*b*) the weight of the excess (unreacted portion) of this element, (*c*) the weight of ferrous sulfide that is formed. (The equation is $Fe + S \rightarrow FeS$.)

CHAPTER III

OXYGEN, VALENCE

Oxygen is the first of the elements to be considered because it constitutes about 50 per cent of all terrestrial matter and because it is essential for the existence of all life.

1. Uses of Oxygen. In the natural decay of dead animal and vegetable matter, oxygen is an important element. The physician administers oxygen to the pneumonia patient to aid in respiration. The aviator must carry a supply of oxygen when flying at high altitudes. In the welding and cutting of metals, oxygen is mixed with acetylene gas to produce the intensely hot flame required. A large number of elements in combination with oxygen form compounds called *oxides*, many of which are very useful substances.

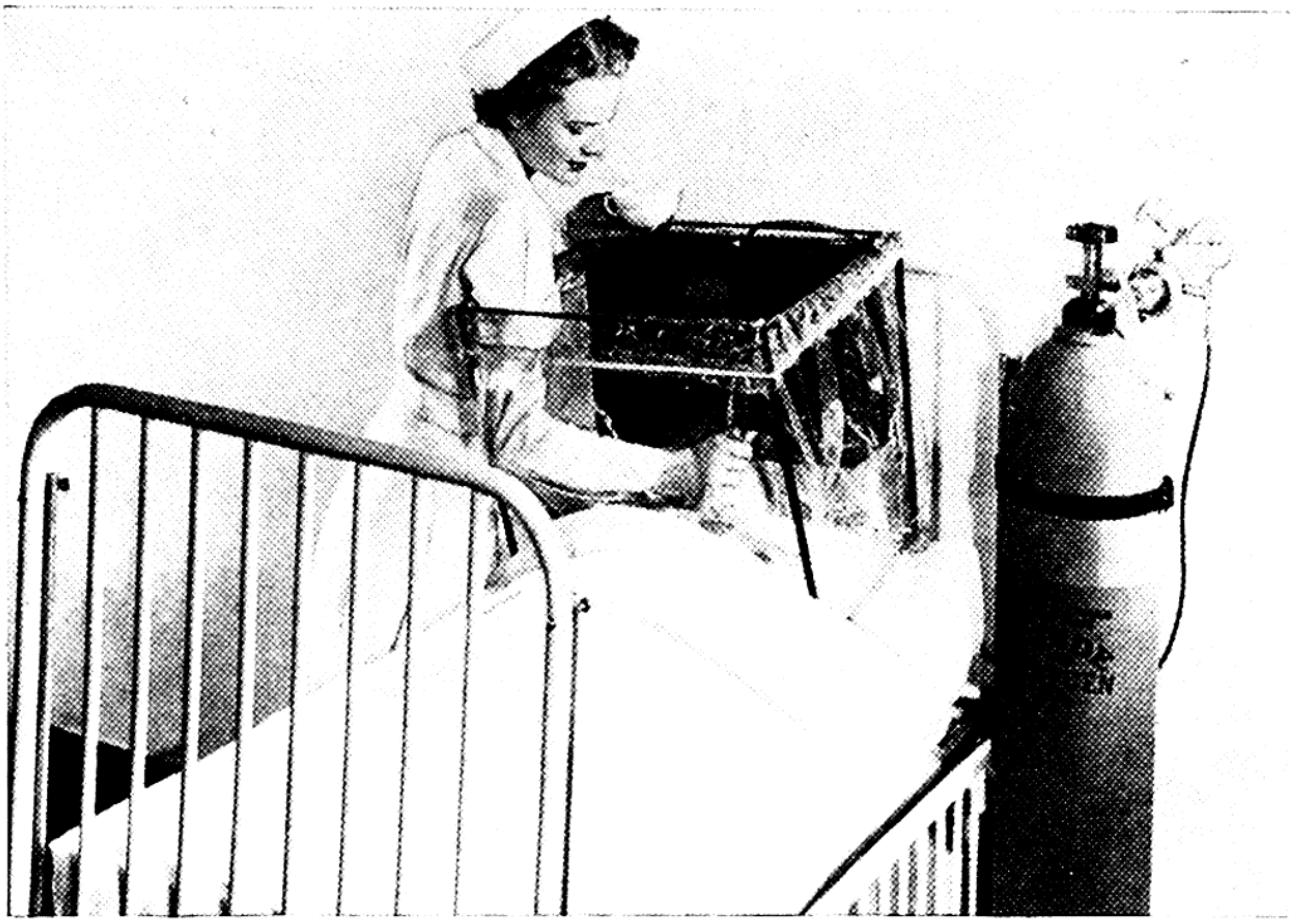

FIG. 1. Use of oxygen in the hospital. (*Linde Air Products Co.*)

2. History of Oxygen. Joseph Priestley, an Englishman, is generally given the credit for the discovery of oxygen (1774) by the decomposition of mercuric oxide. Other investigators (Mayow, Scheele, Lavoisier, and others) had studied it in the earlier years of the eighteenth century. In addition to his scientific work, Priestley devoted much of his time to writing in the fields of philosophy and religion. His later years were spent at the beautiful home that he built at Northumberland, Pa., where a museum was erected to preserve some of his books and apparatus (Fig. 2).

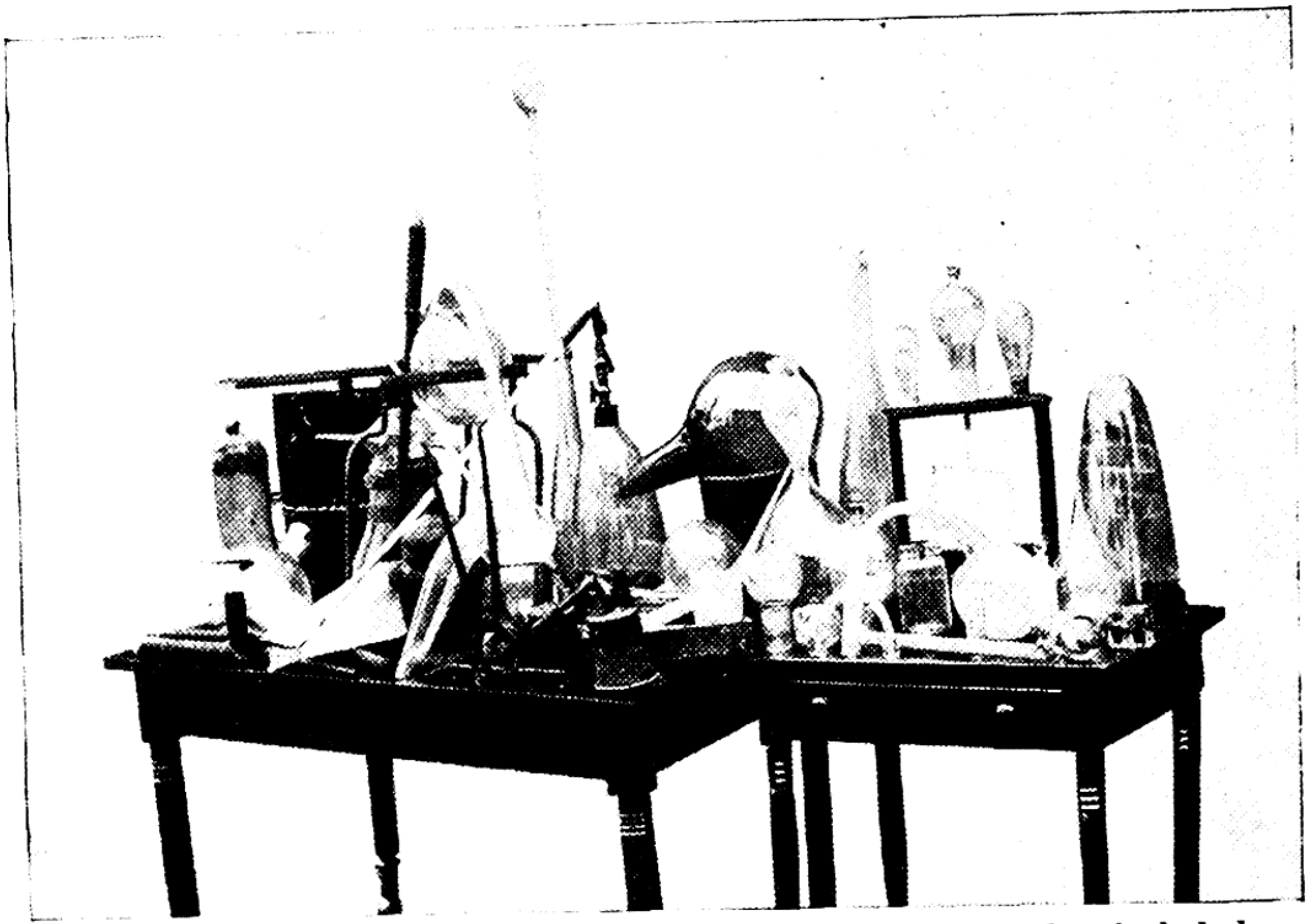

FIG. 2. Some of Joseph Priestley's apparatus, including a chemical balance. *(Courtesy of Dr. Frank C. Whitmore)*

3. Industrial Preparation of Oxygen. Pure oxygen is usually prepared by the liquefaction of air, followed by fractional distillation of the liquid air to separate the nitrogen from the oxygen. The pure oxygen obtained is usually compressed into small steel cylinders at a pressure of about 1,800 lb. per sq. in.

4. Laboratory Preparation of Oxygen. Oxygen may be prepared in small quantities by the electrolysis of water (see Chap. V) or by the thermal decomposition of certain compounds, *e.g.*, potassium chlorate, mercuric oxide, or lead dioxide. Sodium peroxide reacts with water and forms oxygen and sodium hydroxide. The equations for these reactions are shown in Sec. 6, in skeleton and in balanced form. The test for oxygen is done by the so-called *splint test.* If a glowing splint of wood is placed in an atmosphere containing a high percentage of oxygen gas, the splint bursts into flame.

5. Chemical Formula for Oxygen. The formula O_2 is used to represent oxygen in the free state because it can be shown that the oxygen atoms are united in pairs to form oxygen molecules. One may write O for oxygen in an unbalanced or skeleton equation (see below), but in the final or balanced equation oxygen must be written O_2. This does not apply to oxygen in compounds, but only to the element in the free state.

6. Equations. *Skeleton Equations and Balanced Equations.* The formation of a balanced chemical equation involves two steps: (1) writing the correct skeleton equation and (2) balancing the skeleton equation.

The first groups of equations encountered are those representing the various methods for preparing oxygen gas in the laboratory, and these may be used as illustrative examples. The skeleton equations are given in the left-hand column and the balanced equations in the right-hand column of Table I. The skeleton equation merely gives the formulas (or symbols) of the substances used and produced. The balanced equations are not to be memorized but can be obtained from the skeleton equations by the process of balancing the skeleton equations.

TABLE I

EQUATIONS FOR THE PREPARATION OF OXYGEN

Skeleton Equations	*Balanced Equations*
1. The effect of heat* on potassium chlorate:	
$KClO_3 \xrightarrow[\text{(catalyst)}\dagger]{MnO_2} KCl + O$	$2KClO_3 \xrightarrow[\text{(catalyst)}]{MnO_2} 2KCl + 3O_2$
2. The effect of heat* on mercuric oxide:	
$\underset{\text{mercuric oxide}}{HgO} \rightarrow \underset{\text{mercury}}{Hg} + O$	$2HgO \rightarrow 2Hg + O_2$
3. The effect of heat* on lead dioxide (lead peroxide):	
$\underset{\text{lead dioxide}}{PbO_2} \rightarrow \underset{\text{lead monoxide (litharge)}}{PbO} + O$	$2PbO_2 \rightarrow 2PbO + O_2$
4. The reaction of water with sodium peroxide:	
$\underset{\text{sodium peroxide}}{Na_2O_2} + H_2O \rightarrow \underset{\text{sodium hydroxide}}{NaOH} + O$	$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$

* It is not necessary to indicate the heat in the chemical equation.

† For a definition of the term *catalyst*, see Sec. 17.

Meaning of the Balanced Equation. A balanced equation is intended to give a statement of all the molecules and atoms present before and after a chemical change. The first equation in Table I fails to give a complete statement since 3 oxygen atoms are indicated on the left-hand side of the arrow but only 1 oxygen atom appears on the right.

Procedure for Balancing and Completing a Skeleton Equation. The skeleton equation is converted into the balanced equation in the following manner:

a. Note that, if the skeleton equation is changed to

$$KClO_3 \rightarrow KCl + 3O$$

the equation will balance because there are as many atoms of each element on the right of the arrow as on the left. This equation is still incomplete because it indicates that the oxygen produced consists of individual oxygen atoms uncombined with one another. Actually it is known that the oxygen atoms are joined in pairs to form molecules containing 2 oxygen atoms in each molecule. This necessitates a further step:

b. Doubling the entire equation gives

$$2KClO_3 \rightarrow 2KCl + 6O$$

which may be written

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

to give the complete equation for the reaction.

To summarize, the equation goes through the following stages:

(1) $KClO_3 \rightarrow KCl + O$ (skeleton equation)
(2) $KClO_3 \rightarrow KCl + 3O$
(3) $2KClO_3 \rightarrow 2KCl + 6O$
(4) $2KClO_3 \rightarrow 2KCl + 3O_2$ (balanced equation)

The second of the equations listed in Table I is balanced in the same way, but the process is even simpler:

$HgO \rightarrow Hg + O$ (skeleton equation)
$2HgO \rightarrow 2Hg + O_2$ (balanced equation)

The third equation in Table I is balanced in a similar manner:

$PbO_2 \rightarrow PbO + O$ (skeleton equation)
$2PbO_2 \rightarrow 2PbO + O_2$ (balanced equation)

The fourth equation in Table I is slightly more complicated (II 5):

$Na_2O_2 + H_2O \rightarrow NaOH + O$ (skeleton equation)
$Na_2O_2 + H_2O \rightarrow 2NaOH + O$
$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$ (balanced equation)

Obviously, after some practice the various steps can be combined and the final equation written in one step.

7. Importance of Correct Formulas and Correct Skeleton Equation. It cannot be too strongly emphasized that the correct formulas of all starting materials and products must be known before attempting to balance an equation. Thus the skeleton equation must be memorized before attempting to balance it. Chemists and advanced students can often work out a correct skeleton equation, but this is possible only because they have learned a considerable number of skeleton equations some of which are closely related to the one being worked out. In fact, after a little study, beginning students can do this for certain types of chemical changes. Such procedures are always subject to error. In the future, absolutely certain methods of predicting the results of experiments may be developed, but at present the writing of correct equations requires a knowledge of skeleton equations or the experiments upon which these equations are based.

Exercise

1. Copy the skeleton equations in Table I. Close the book and balance the equations as correctly as possible without reference to the book. Then compare your balanced equations with those in the book.

8. Directions for Study. It is of greatest importance that all exercises be carried out in a thorough and conscientious manner since a working knowledge of equations is a necessary requirement for effective and satisfactory progress in the study of chemistry.

9. Physical Properties of Oxygen. In chemical work, an element or compound is described by listing its physical and chemical properties. The meaning of these terms can be made clear by examples. Thus, the element oxygen may be described by indicating that it has the following physical properties:

a. It is a gas at ordinary temperature and pressure.
b. It is colorless, odorless, and tasteless.
c. It is somewhat but not largely soluble in water.
d. It is slightly heavier than air.

In a great many cases, physical properties can be expressed in numerical form. For instance, the solubility of oxygen in water is about 3 volumes of oxygen in 100 volumes of water (at ordinary temperature and pressure). Such numerical values are obtained from reference books when needed.

It is to be noted that none of the above physical properties involve any chemical changes. Physical properties include only those characteristics and qualities of a substance which do not involve any chemical change of the substance.

It is to be clearly recognized that the above facts refer only to oxygen in the free state, when uncombined with other elements. When oxygen is united with other elements as in $KClO_3$ or HgO, none of the above properties are noticeable. An element exhibits its own properties only when it is uncombined with other elements. In compounds, the properties of the element are generally not in evidence, each compound having its own individual properties. This point may be illustrated by comparing the properties of oxygen with the properties of some of its compounds.

10. Chemical Properties of Oxygen. The complete description of any substance always includes its chemical properties. Chemical properties are simply the chemical changes that a substance will undergo. The chemical properties of oxygen may be summarized by stating that oxygen has a marked tendency to combine with other elements and with compounds, especially when heated. Specific examples of the chemical properties of oxygen are that it unites with hot sulfur to form sulfur dioxide, and also with hot phosphorus to form phosphorus pentoxide. Iron burns at high temperatures to form a black oxide of iron, and rusts at ordinary temperatures to form a red oxide. Carbon forms carbon dioxide if it burns with a plentiful supply of oxygen, and carbon monoxide is formed if there is a deficient supply of oxygen or air. These and other examples are summarized by the following equations:

ACIDIC OXIDES (OXIDES OF NONMETALS)

$S + O_2 \rightarrow SO_2$ (gas)
$C + O_2 \rightarrow CO_2$ (gas)
$2C + O_2 \rightarrow 2CO$ (gas)
$4P + 5O_2 \rightarrow 2P_2O_5$ (white solid)

BASIC OXIDES (OXIDES OF METALS)

$2Mg + O_2 \rightarrow 2MgO$ (white solid)
$2Ca + O_2 \rightarrow 2CaO$ (white solid)
$3Fe + 2O_2 \rightarrow Fe_3O_4$ (black solid)
(burning)
$4Fe + 3O_2 \rightarrow 2Fe_2O_3$ (red solid)
(rusting)
$2Na + O_2 \rightarrow Na_2O_2$ (light yellow solid)

Exercise

2. For each of the above equations, indicate the name of the oxide formed.

11. Acidic Oxides and Basic Oxides. *An acidic oxide is an oxide that, when combined with water, forms an acid. A basic oxide is* *an oxide that, when combined with water, forms a base or hydroxide.* A considerable number of oxides cannot be easily tested as acidic or basic, because they do not combine directly with water. Those oxides that do combine directly with water may be classified by testing the resulting solution with litmus paper, which turns red in an acid solution, blue in a basic solution. The reactions of oxides with water are represented by the following equations:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad \text{(sulfurous acid)}$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \qquad \text{(phosphoric acid)}$$
$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad \text{(carbonic acid)}$$
$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(calcium hydroxide)}$$
$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad \text{(magnesium hydroxide)}$$
$$BaO + H_2O \rightarrow Ba(OH)_2 \qquad \text{(barium hydroxide)}$$

12. Metals and Nonmetals. Elements may be divided into two major classes: *metals* (metallic elements) and *nonmetals* (nonmetallic elements). Metals can usually be recognized by their metallic luster, relatively great density, and high conductivity of heat and electricity. They also combine with oxygen to form basic oxides while nonmetals form acidic oxides.

Exercise

3. List separately the metals and nonmetals in the oxides of Sec. 11.

13. Acids. An acid may be described as a compound whose water solution tastes sour and turns litmus red. All acids contain hydrogen and a nonmetal, and often oxygen as well. The symbol for hydrogen conventionally appears first in the formula. Examples of acids are sulfurous acid, H_2SO_3; phosphoric acid, H_3PO_4; carbonic acid, H_2CO_3.

14. Bases or Hydroxides. A soluble base or hydroxide may be described as a compound whose water solution tastes bitter, feels slippery, and turns litmus blue. Many bases are not soluble in water. The formula of a base contains a metal and the hydroxide (OH) group or radical. Examples are sodium hydroxide, $NaOH$; calcium hydroxide, $Ca(OH)_2$; magnesium hydroxide, $Mg(OH)_2$; aluminum hydroxide, $Al(OH)_3$.

15. Kinds of Chemical Changes. The brief study of oxygen already made has introduced several varieties of chemical change. *Decomposition* is the change of one substance into two or more other substances. *Combination* is the union of two or more substances into one substance. *Oxidation* is a change in which oxygen combines with some other substance. *Combustion* is a change accompanied by liberation of light and heat. *Reduction* is a change in which a compound loses some or all of its oxygen. The terms *oxidation* and *reduction* are also used in a broader sense, which will be discussed later (XI. 10).

Exercise

4. Give one example of each of the above kinds of chemical change and write the equation for this change.

16. Oxidation. Oxidation is closely related to combustion. Sometimes it takes place with extreme rapidity, as in the explosion of a flashlight powder or a flashlight bulb; in other cases, the action is very slow as in the rusting of iron, in the slow rotting of wood, or in animal respiration. Almost all combustion reactions are cases of rapid oxidation.

17. Catalysts and Catalysis. In the preparation of oxygen from potassium chlorate (Table I), it is found by experiments that the reaction proceeds much more rapidly if a small amount of a catalyst (MnO_2 or Fe_2O_3) is previously mixed with the potassium chlorate. It can also be shown experimentally that the oxygen comes from the potassium chlorate and not from the catalyst. *A catalyst (catalytic agent or contact agent) is any substance that changes the rate of a chemical reaction, without undergoing permanent change in its composition.* If the rate of the reaction is increased, as in the case of the decomposition of potassium chlorate catalyzed by manganese dioxide, the manganese dioxide is known as a *positive catalyst.* Substances are sometimes used as *negative catalysts* or *inhibitors* to decrease the rate of reactions; for example, certain rust inhibitors are added to antifreeze liquids used in automobile radiators.

It is not to be assumed that a catalyst for one chemical reaction will catalyze all other reactions. A catalyst is specific in its action, *i.e.*, effective for a certain reaction or at most for a few similar reactions.

18. Ozone. When subjected to certain types of electric discharge, ordinary oxygen gas changes into ozone. This is a different form of pure oxygen composed of molecules each containing 3 oxygen atoms, O_3. The different type of molecule results in markedly different properties such as a sharp odor and great chemical activity. Ozone changes rapidly into ordinary oxygen on standing.

Exercise

5. Write the equation for the change of ozone, O_3, to ordinary oxygen, O_2.

19. Valence. The formulas of the oxides of elements indicate varying numbers of atoms; *e.g.*, H_2O, HgO, Fe_2O_3, CO_2, etc. It appears that the elements have the property of combining in varying proportions. Other compounds, *e.g.*, chlorides of elements, exhibit a similar relationship as illustrated by HCl, $HgCl_2$, $FeCl_3$, CCl_4. The term *valence* is used in connection with this combining capacity of the elements. *The valence of an element is the number of atoms of hydrogen or of chlorine that will combine with one atom of that element.*

20. Radical. Elements often react together as groups known as *radicals; e.g.*, SO_4, NO_3, OH, CO_3, PO_4, are radicals in the compounds H_2SO_4, HNO_3, $NaOH$, H_2CO_3, H_3PO_4. *A radical is a group of atoms that acts as a single atom.*

21. Valence Number. In order to write formulas correctly, it is necessary to memorize the valence numbers of the common elements and radicals. The valence numbers quite generally used are listed in Table II. A discussion of the fundamental theory of valence is presented in Chap. IX.

TABLE II

VALENCE NUMBERS

Radicals, *e.g.*, in Na_2SO_4, $KClO_3$

1+	2+	3+	4+	5+	1−	2−	3−
H^+	Mg^{2+}	Al^{3+}	$C^{4+ \text{ or } 4-}$	N (variable)	OH^-	O^{2-}	PO_4^{3-}
Na^+	Ca^{2+}	B^{3+}	$Si^{4+ \text{ or } 4-}$	P (variable)			
K^+	Ba^{2+}			As (variable)	Cl^-	SO_4^{2-}	AsO_4^{3-}
Ag^+	Zn^{2+}				ClO_3^-	CO_3^{2-}	
Cu^+					NO_3^-		
NH_4^+	Cu^{2+}						
Hg^+	Hg^{2+}						
	Fe^{2+}	Fe^{3+}					
	Sn^{2+}		Sn^{4+}				
	Pb^{2+}		Pb^{4+}				

Exercises

6. Without reference to Table II, write empirical formulas for the oxides of Na, Mg, Al, Sn, P.

7. Without reference to Table II, write empirical formulas for compounds of the SO_4 (sulfate) radical with Ag, Ca, Mg, Al, Fe.

NOTE: The total + valence numbers in a correct formula always equal the total − valence numbers; *e.g.*, in $Fe_2(SO_4)_3$, $2(3+)$; $3(2-)$, or $Fe_2^{6+}(SO_4)_3^{6-}$.

8. Write skeleton and balanced equations for the reaction of oxygen with (*a*) zinc, (*b*) calcium, (*c*) lead, (*d*) tin. If an element has several valences, write an equation to correspond to each valence.

9. If 12.2 g. potassium chlorate is decomposed by heat, calculate (*a*) the weight in grams of oxygen produced and (*b*) the weight in grams of potassium chloride formed.

10. Calculate (*a*) the weight of Fe_3O_4 formed by the combustion of 55 g. iron in excess of oxygen and (*b*) the weight of oxygen used in this reaction.

11. What percentage of the total oxygen content is released in the decomposition (by heat) of each of the following compounds: (*a*) potassium chlorate, (*b*) mercuric oxide, (*c*) lead dioxide?

SUGGESTED READING

Browne, Priestley's Life in Northumberland. *J. Chem. Education*, **4**, 159 (1937).
Carter and Reinhard, Modern Uses of Oxygen. *J. Chem. Education*, **19**, 91 (1937).
Ficklen, Dust Explosions, *J. Chem. Education*, **19**, 131 (1942).

CHAPTER IV

GASES. THE KINETIC THEORY

The practical use of gases in industry is so extensive that it is important for us to consider some of their properties and the laws that relate to these properties. The study of oxygen, a typical gas, has just been concluded. A few of the practical uses of gases are listed below.

1. Gases in Industry. *Oxygen.* Compressed oxygen is stored in steel cylinders at very high pressure and used in the cutting and welding of metals and for hospital purposes. (Why is oxygen stored under high pressure?)

Compressed air is required in the operation of air brakes, rock drills, and riveting machines and in the excavation of tunnels. Certain types of agricultural sprayers also make use of compressed air.

Steam. All the various types of steam engines depend for their operation upon the power generated by steam under high pressure.

Fuel gases, e.g., coal gas, natural gas, and water gas, are usually delivered under pressure to the place of consumption.

Refrigerating Gases. For kitchen refrigerators, for meat-packing plants, and for fruit cold-storage rooms, various gases are used, *e.g.*, ammonia, carbon dioxide, Freon, and sulfur dioxide. The choice of a suitable gas for a given type of refrigerator depends upon the temperature and pressure required for liquefaction (*e.g.*, critical temperature and pressure) and other factors. A more complete discussion of refrigeration is included in the study of ammonia.

2. Properties. Gases have many properties that are distinctly different from those of liquids and solids. One of them is that the volumes of all gas samples change in almost exactly the same way with pressure and with temperature changes regardless of the chemical composition or purity of the gas. The following statements (gas laws) are generally true for all gas samples if the pressure is not extremely high and if the temperature is not too near the temperature of liquefaction.

3. Variation of Volume with Pressure. Boyle's law states that *the volume of a sample of gas varies inversely with the pressure, if the temperature remains constant.* Thus, increase in pressure causes decrease in volume of the gas sample, and vice versa. (Refer to Sec. 7 for details of pressure measurement.)

$$V \propto \frac{1}{P}$$

4. Variation of Volume with Temperature. Charles's law states that *the volume of a sample of gas varies directly with the absolute temperature, if the pressure remains constant.* Thus, increase in temperature causes increase in volume of the gas sample, and vice versa or,

$$V \propto T \text{ (abs.)}$$

Absolute temperatures are obtained by adding 273* to the centigrade temperature; thus,

$$T^\circ \text{ abs.} = \pm{}^\circ\text{C.} + 273$$

(See Appendix, Table II.)

5. Partial Pressures. Dalton's law of partial pressures states that *the sum of the individual or partial pressures of the various gases in a mixture of gases is equal to the total pressure of the mixture*, or,

$$P = p_1 + p_2 + p_3 \cdot \cdot \cdot$$

If oxygen is collected by water displacement, the gas in the bottle is not pure oxygen but a mixture of oxygen and water vapor. The total pressure of such a sample is the sum of the individual pressures of the oxygen and the water vapor. To obtain the pressure of the oxygen alone, it is necessary to subtract the pressure of the water vapor from the total pressure.

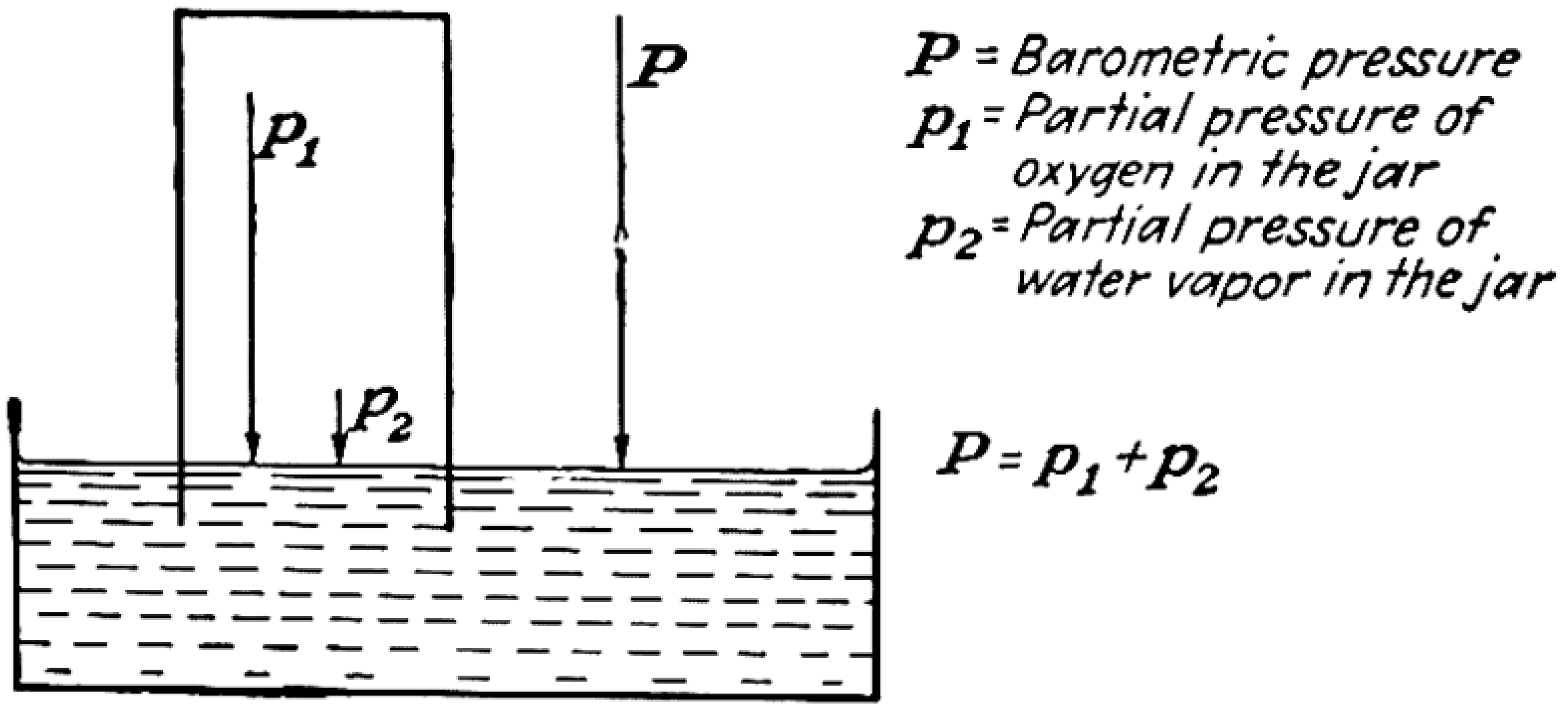
P
p_1
p_2
P = Barometric pressure
p_1 = Partial pressure of oxygen in the jar
p_2 = Partial pressure of water vapor in the jar
$P = p_1 + p_2$

FIG. 1. Application of Dalton's law in the case of oxygen in a jar inverted over water.

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* The number 273 is based on the fact that, when a known volume of a gas at 0°C. is heated 1°C., it expands $\frac{1}{273}$ of its volume; heated to 10°C., it expands $\frac{10}{273}$ of its volume; etc. The fraction $\frac{1}{273}$ is known as the *coefficient of expansion of a gas.*

6. Diffusion. Graham's law of diffusion states that *the rate of diffusion of a gas is inversely proportional to the square root of its density*, or,

$$r \propto \frac{1}{\sqrt{d}}$$

Thus, the lighter a gas is, the greater its speed in passing through a porous wall.

7. Measuring the Pressure of a Sample Gas. A basic method for measuring the pressure of a sample of gas is to determine the height of the mercury that the gaseous pressure will support. This may be illustrated by describing the method used to determine the pressure of the atmosphere. This is done by completely filling a barometer tube with mercury and then placing the tube, open end down, in another open vessel of mercury. When the stopper is removed from the mouth of the tube, the mercury will fall until the pressure of the remaining column of mercury is just equal to the pressure exerted by the surrounding air on the surface of the mercury in the open vessel. Such an arrangement is called a *barometer*. There is a vacuum above the mercury inside the barometer tube and therefore no pressure on this surface of mercury.

At sea level, the pressure of the atmosphere is sufficient to support a column of mercury about 29.9 in. (760 mm.) high. At other locations, the air pressure is less in proportion to the altitude above sea level, and so the height of the mercury column of the barometer will, accordingly, be less in the same proportion. In any one location, the pressure of the mercury column of the barometer will vary in a similar manner. For altitudes up to several thousand feet, the barometric column drops about 1 in. for each 1,000 ft. of increase in altitude. At higher altitudes, ranging into the stratosphere, the variation is more complex.

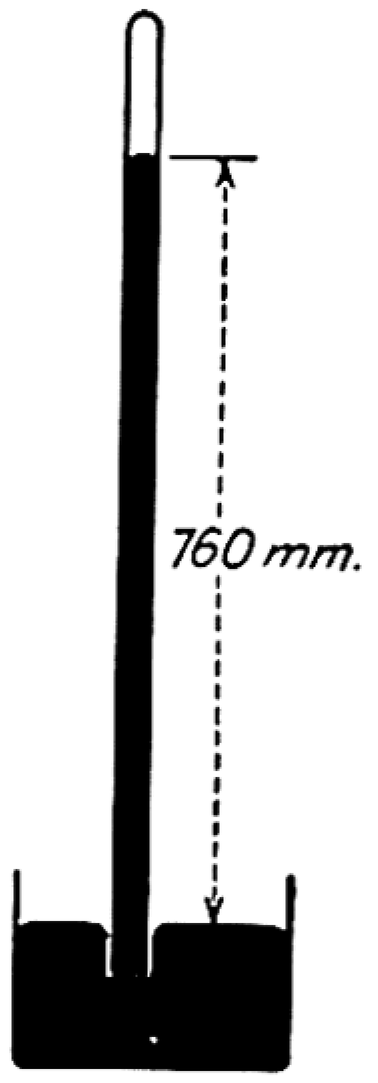

FIG. 2. Mercurial barometer.

The pressure of the gas in a closed pipe or tank may be measured by a similar method. In this case, the open vessel at the base of the barometer must be replaced by a closed one and a connection made from this closed vessel to the pipe or tank. The gas in the pipe or tank then exerts its pressure on the surface of the mercury, and a column of mercury, of height proportional to the pressure, will be supported. Such an arrangement is called a *manometer*. If the pipe or tank is connected to a vacuum pump and if some of the gas is removed and its pressure thus decreased, the height of the mercury column will decrease. At all times the height of the mercury column is a measure of the gas pressure in the attached container.

Spring gauges are used in many instances to measure gaseous pressure, but they must always have their scales properly marked by a process that involves comparison of the spring gauge with a barometer or manometer, or a similar device.

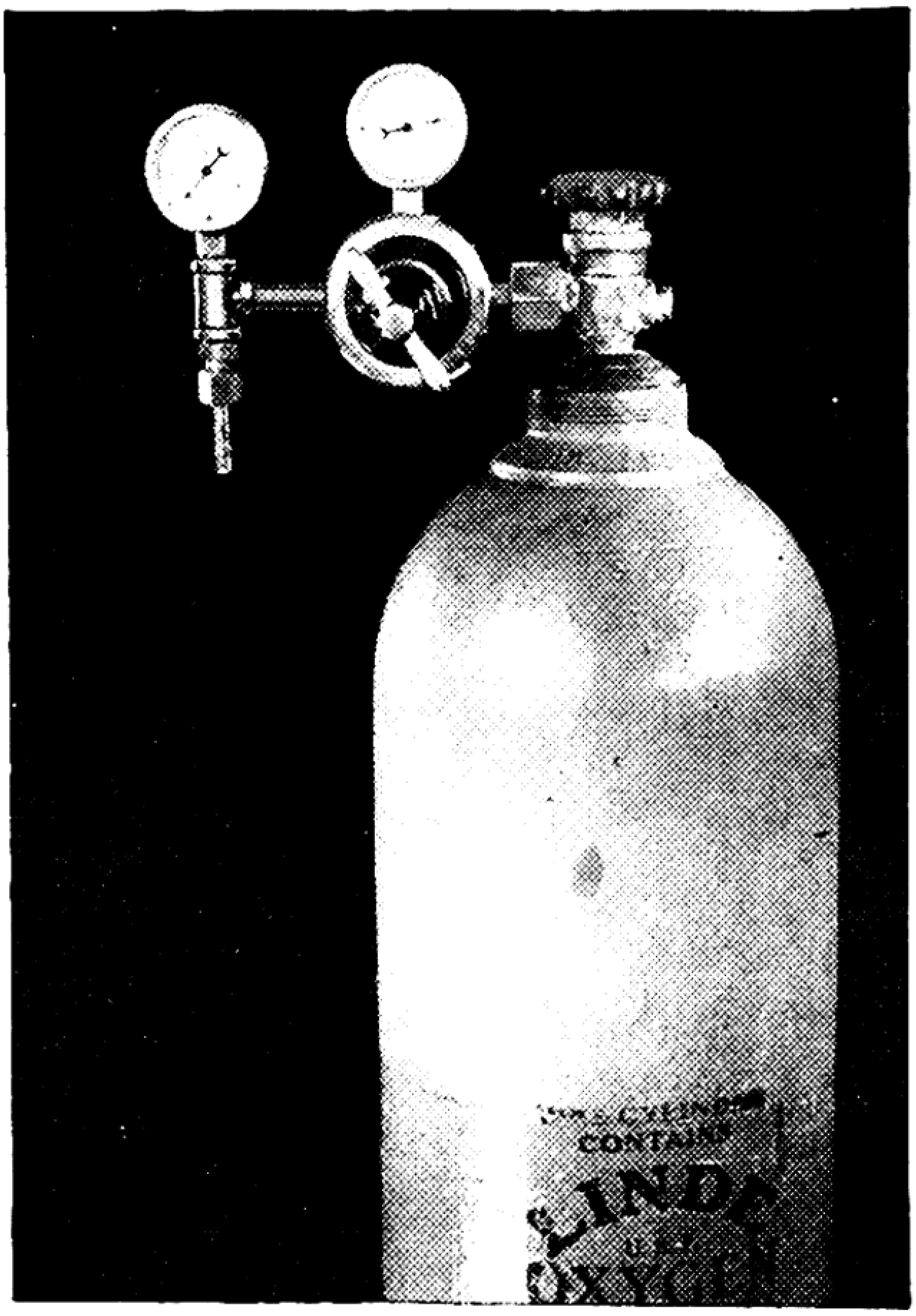

Fig. 3. Pressure regulator and gauges. (*Linde Air Products Co.*)

None of the methods described above is satisfactory for the measurement of the pressure of gas samples collected in bottles inverted over mercury, water, or some other confining liquid. Such samples will always be under approximately atmospheric pressure. The exact pressure can be determined by adjusting the bottle until the level of the confining liquid inside the bottle is the same as the outside level. The pressure inside will then be identical with the pressure of the air outside, and the latter can be measured by means of a barometer.

For the above reasons, the pressure of an ordinary sample of gas is usually expressed in millimeters of mercury or inches of mercury. The *standard pressure* is the normal air pressure at sea level or 760 mm. mercury. This is 29.9 in. mercury, 1 atm. of pressure, or approximately 14.7 lb. per sq. in. A highly compressed gas exerting 100 times the standard pressure would be referred to as being at a pressure of 100 atm.

Exercises

1. Express in atmospheres a pressure of (*a*) 1,520 mm., (*b*) 132.3 lb. per sq. in.
2. Express in millimeters a pressure of (*a*) 3 atm., (*b*) 0.1 atm.
3. Chlorine gas is converted to a liquid at 18°C. and at a pressure of 6.5 atm., and is shipped in tank cars. What would be the pressure in pounds per square inch in the tank cars?
4. What is the partial pressure of oxygen gas collected over water at a total pressure of 740 mm. when the water-vapor pressure is 15 mm.?
5. Will the pressure of a sample of gas collected over water be greater or less than if the same sample were collected dry?

8. Gas Calculations. It is often necessary to know how much the volume of a given sample of gas would increase or decrease if its temperature and pressure were changed to some new values. The new volume can usually be calculated simply by use of the relation:

$$\left(\begin{matrix}\text{New}\\\text{volume}\end{matrix}\right) = \left(\begin{matrix}\text{original}\\\text{volume}\end{matrix}\right) \times \frac{\text{(one temperature)}}{\text{(other temperature)}} \times \frac{\text{(one pressure)}}{\text{(other pressure)}}$$

The following example will indicate how Boyle's, Charles's, and Dalton's laws and simple reasoning may be used in calculating the new volume.

Example. A quantity of oxygen collected in a bottle over water measured 500 cc. at 25°C. and 755 mm. Calculate the volume of the oxygen at S.T.P. (S.T.P. means standard temperature and pressure of 273° abs. or 0°C., and 760 mm. S.C., or standard conditions, has the same meaning.)

TABULATION OF DATA

	Original conditions	New conditions	Reasoning
Volume	500 cc.	V cc.	
Temperature	25°C. 298° abs.	0°C. 273° abs.	Decrease in temperature causes decrease in volume; therefore, multiply 500 cc. by fraction $^{273}/_{298}$
Pressure	755 − 23.5 mm. or 731.5 mm.	760 mm.	Increase in pressure causes decrease in volume; therefore, multiply 500 cc. by fraction 731.5/760

Numerical statement:

$$500 \text{ cc.} \times \frac{273}{298} \times \frac{731.5}{760} = V \text{ at } 0^\circ\text{C. and } 760 \text{ mm.}$$

It is to be observed that three steps are used in solving this problem:

The first step is a systematic tabulation of the information given. The values of volume, temperature, and pressure are indicated for the original and the new conditions. The new volume is, of course, unknown and indicated merely by V. The centigrade temperature is converted to the absolute scale.

Since the oxygen was collected over water, it is mixed with water vapor. Therefore, the pressure of vapor (23.5 mm. at 25°C.) is subtracted from the total pressure (755 mm.) in order to get the actual pressure of the oxygen (731.5 mm.). The vapor pressure of water has a definite fixed value for each temperature and a table of such values is found in the Appendix of this book, in handbooks, and in laboratory manuals. This water-vapor correction must always be made when the gas is collected over water, but not otherwise.

The second step involves a decision as to which temperature and which pressure are to be used in the numerator of the fractions in the calculation. This is determined by reasoning based on Boyle's and Charles's laws, as indicated in the example. If the reasoning concerning the temperature change indicates that the new volume will be smaller than the original, then the original volume must be multiplied by a fraction that has the smaller number above and the larger number below. Thus, in the example, the fraction $^{273}/_{298}$ is used rather than $^{298}/_{273}$. The same idea holds true for the pressure change. It is especially to be noted that the pressure change is entirely ignored in the reasoning concerning temperature and vice versa.

The third step consists of writing in statement form the value of the new volume. In general, it is not necessary at this point to do the numerical calculation unless some use is to be made of the answer, since the purpose in stating these problems is to learn how the gas laws are applied and to follow through the reasoning involved. It is not advisable to employ the equations usually given in textbooks. Substitution of data in a formula or equation may become merely a mechanical process and does not ensure a thorough understanding of the gas laws and their applications.

To understand thoroughly the above type of calculation it is necessary to work out a number of problems such as the following. In these exercises, temperature must be converted to absolute scale, but pressure and volume may be used in any units provided the same units are used throughout each exercise. Thus, it is incorrect to express original pressure in millimeters and new pressure in atmospheres; if the original volume is tabulated as cubic centimeters (cc.), the new volume must necessarily be in the same unit.

Exercises

6. Show how to calculate the volume at standard conditions of 90 cc. gas collected over water at 17°C. and 740 mm.

7. Show how to calculate the volume of 150 cc. gas at 240°C. and 289 mm. if the temperature is changed to 20°C. and the pressure to 730 mm.

8. Show how to calculate the volume of 100 cc. gas at 17°C. and 770 mm., if conditions are changed to 0°C. and 760 mm.

9. Calculate the volume, at standard conditions, of 187 cc. hydrogen collected over water at 25°C. and 745 mm. pressure.

10. Calculate the volume at standard conditions of 560 cc. gas collected over water at 15°C. and 750 mm. pressure. If 1 l. of the gas weighs 0.09 g. at S.C., find the weight of the above sample of gas. (1 l. = 1,000 cc.)

9. Deviations from the Gas Laws. Careful experiments have shown that gases do not follow the gas laws exactly. The differences or deviations are very slight unless the gas is under high pressure or is near liquefaction conditions. Under such conditions, the deviations are important and must be considered in engineering problems involving gases. The deviations from Boyle's law are of two kinds: (1) at low pressures, gases are more compressible than Boyle's law predicts; (2) at high pressures, they are less compressible.

10. Perfect Gas. An imaginary gas that shows no deviations is referred to as a perfect or ideal gas. Boyle's and Charles's laws are often called *perfect-gas laws.*

11. Liquefaction of Gases, Critical Temperature, Critical Pressure. At ordinary pressure a gas may be liquefied by sufficient cooling. A gas may be liquefied also by sufficient increase in pressure if, and only if, it is below a definite temperature. This temperature (the critical temperature) varies considerably for different gases. For oxygen it is −119°C., for hydrogen −240°C., for carbon dioxide +31°C., for water vapor +374°C. *Critical temperature* is the temperature above which a gas cannot be liquefied by pressure alone. *Critical pressure* is the pressure necessary to liquefy a gas at the critical temperature.

Exercise

11. The critical temperature of carbon dioxide is 31°C. What does this mean?

12. Basic Principles of the Kinetic Theory of Gases. All the properties of gases can be explained if one assumes that gases are composed of small particles called *molecules* and that these molecules behave as follows:

a. The molecules are in rapid motion.

b. The molecules are very small and very numerous.

c. The energy of attraction between molecules is very small compared with the energy of motion.

d. Collisions between molecules take place without loss of energy.

e. Molecules are small in comparison with the distances between them.

f. Increase in temperature causes increase in speed of the molecules.

g. Gaseous pressure is due to the bombardment of the molecules on the walls of the container.

It is to be observed that none of the basic ideas of the *kinetic theory* (molecular hypothesis) admit of proof by direct observation. Since molecules cannot be observed, no direct test of the theory is possible. The theory does, however, explain a great many properties of gases and, as long as it does so, it is a satisfactory theory.

13. Explanation of the Properties of Gases by Means of the Kinetic Theory. *a.* To explain gaseous pressure, it is assumed that the molecules are in rapid motion and that their bombardment of the walls of the container causes the gaseous pressure.

b. To explain the uniformity of pressure in all directions and on all surfaces at all times, it is assumed that the molecules are very small and very numerous (about 6×10^{23} per cubic foot).

c. To explain the great compressibility of gases, it is assumed that the molecules are small compared with the distance between them.

d. To explain the ability of a gas to fill any container, it is assumed not only that the molecules are in motion but that their energy of attraction is very small compared with the energy of motion and, therefore, there is little cohesion between molecules.

e. To explain the absence of settling in a gas, it is assumed that molecular collisions take place without loss of energy (elastic collisions). Thus, the speed and energy lost by 1 molecule in a collision must be gained by another molecule, and the average speed and total energy remain unchanged.

f. To explain the behavior of gases when heated (Charles's law), it is assumed that the increase in temperature causes an increase in the speed of the molecules. Thus, if a sample of gas is heated in a closed container, the molecules will travel back and forth between the walls more rapidly, will strike the walls more often and with more energy, and as a result the pressure in the container will increase. If the pressure, *i.e.*, the number of collisions with the walls, is to be kept constant, the size (volume) of the container must be increased so that the molecules have farther to travel between collisions with the walls. This is, of course, a statement of Charles's law: the volume of a gas increases if temperature is increased and pressure held constant.

g. The liquefaction of gases on cooling is due to a gradual decrease in energy of motion until the attractive forces between molecules can increase cohesion. Ease of mixing of gases is due to the motion of molecules and the large free space between them.

Exercises

12. Use the kinetic theory to explain why a tin can collapses if the air is pumped out of it with a vacuum pump. Do not use the words *pressure* or *vacuum* in your explanation, but consider only the molecular action on the inner and outer surfaces of the can. (A diagram is helpful.)

13. A tin can containing a small quantity of boiling water collapses after its opening is closed, and the can is suddenly cooled. Explain by molecular action.

14. If an automobile tire is inflated to a pressure of 30 lb. per sq. in. at 20°C., what will be the pressure if it is heated to 50°C. by driving the car? (Assume that the volume of the tire remains constant.)

15. The internal diameter of an air pump is 2 in., the stroke is 10 in. Air going into the pump is at 18°C. and 1 atm. After 200 strokes of the pump, what pressure, in pounds per square inch, of air is produced in an attached tank of 2,000 cu. in. capacity, if the compression raises the air temperature to 27°C.? (Draw a sketch. Assume that the air already in the tank is at 1 atm.)

14. Kinetic Theory and Liquids and Solids. The kinetic theory may be easily related to liquids. Basic principles *a*, *b*, *d*, and *f* in Sec. 12 are valid for the molecules of a liquid but *c*, *e*, and *g* are not valid since cohesion between molecules, incompressibility, and inability to fill a container completely are outstanding properties of all liquids. The kinetic theory is not ordinarily applied to solids since, in this case, the freedom of motion of the molecules is known to be so greatly restricted by the attraction of neighboring molecules that, in general, a molecule merely moves back and forth with a vibratory motion.

15. Boyle's Law and the Kinetic Theory. Boyle's law is explained by noting that, if a sample of gas is in a closed container and if the size of the container (volume) is decreased, all the molecules will have shorter distances to travel between collisions with the walls;

therefore, in a given time there will be more collisions with the walls and a higher pressure.

SUGGESTED READING

Timm, The Kinetic Molecular Theory and Its Relation to Heat Phenomena, *J. Chem. Education*, **12,** 31 (1935).

Walthus, The Lowest Temperatures, *J. Chem. Education*, **13,** 172 (1936).

CHAPTER V

HYDROGEN. EQUIVALENT WEIGHT

Hydrogen is of great industrial importance in the production of ammonia, in the hydrogenation (hardening) of vegetable oils, and in the cutting and welding of certain metals and alloys. The properties of hydrogen are of considerable interest, and some of them will now be considered. The various methods of preparing hydrogen will then be presented. In this connection we shall learn more about acids, bases, and salts, and the important concept known as equivalent weight.

1. Occurrence. Although hydrogen is rarely found naturally in the free state, it is an important constituent of many common substances, *e.g.*, water, acids, hydrocarbons, and carbohydrates. Hydrogen means "water former."

2. Physical Properties. Probably the outstanding physical property of hydrogen is its low density (0.09 g. per liter at standard conditions). Not only is it much lighter than air, but it is the lightest known substance. Hydrogen is also, next to helium, the most difficult substance to liquefy, a temperature of about −240°C. being required at 12.8 atm. pressure. Hydrogen also has another unusual property—that of dissolving extensively in certain metals, notably palladium and other related elements. Thus, 1 volume of palladium powder will dissolve 500 volumes of hydrogen at ordinary temperature and pressure. Hydrogen is an odorless, colorless, tasteless gas, with a relatively low solubility in water.

3. Chemical Formula for Ordinary Hydrogen Gas. The formula is written H_2 to signify that hydrogen gas is composed of molecules containing 2 atoms each. In every complete and balanced equation involving hydrogen, the formula H_2 is used. As in the case of oxygen, this applies only to hydrogen in the free state. The formulas of hydrogen compounds may contain 1, 2, or more H atoms, as in HCl, H_2S, NH_3, CH_4. Atomic hydrogen (see Sec. 4) has the simple formula H.

4. Chemical Properties. *Union with Oxygen to Form Water.* This may take place quietly as in a flame, or violently when a mixture of hydrogen and oxygen (or air) is ignited.

$$2H_2 + O_2 \rightarrow 2H_2O$$

The equation is the same whether hydrogen burns or explodes or whether it unites with oxygen of the air or pure oxygen. This reaction occurs with the evolution of considerable heat and is therefore called an *exothermic reaction.* When the production or use of heat by a chemical reaction is of interest or importance, a *thermochemical equation* may be written instead of the ordinary chemical equation.

$$2H_2 + O_2 \rightarrow 2H_2O + 115{,}600 \text{ cal.} \qquad \text{(thermochemical equation)}$$

In many cases, the exact number of calories of heat is not important and the symbol delta, Δ, is used instead. In case several different thermochemical equations are encountered, the symbols Δ_1, Δ_2, etc., are used to distinguish the various quantities of heat concerned. Thus, the above thermochemical equation may be written,

$$2H_2 + O_2 \rightarrow 2H_2O + \Delta_1 \qquad \text{(thermochemical equation)}$$

Formation of Atomic Hydrogen. At 3000°C. hydrogen molecules decompose, so that, by passing ordinary hydrogen gas through an electric arc, atomic hydrogen is produced.

$$H_2 + \Delta_2 \rightarrow 2H$$

This is an *endothermic reaction* because it uses heat. The same reaction may occur when ordinary hydrogen gas comes in contact with certain catalysts and is related to the activity of these catalysts. When atomic hydrogen is used in a suitable torch, combination of hydrogen atoms occurs, and more heat is given off than is produced by the combustion of the same amount of molecular hydrogen. Advantage is taken of this fact in the atomic hydrogen electric-arc-welding process.

$$2H \rightarrow H_2 + \Delta_2 \qquad \left\{\begin{array}{l}\text{thermochemical equation for combination}\\ \text{of atomic hydrogen in atomic arc welding}\end{array}\right.$$

Another advantage of the atomic hydrogen welding torch is that oxygen is not present at the point of the weld and, therefore, the metal does not undergo oxidation.

Exercises

1. Why is it correct to write 2H rather than H_2 in the above equation?
2. Is the above reaction exothermic or endothermic?

Reducing Action of Hydrogen. Hydrogen has the property of reacting with certain oxygen compounds such as oxides in such a way that the compound loses its oxygen, and water is formed by the union of the hydrogen and the oxygen. Thus, hydrogen passed over hot copper oxide results in the production of copper and water.

$$CuO + H_2 \rightarrow Cu + H_2O$$

The hydrogen causes the *reduction* of the copper oxide and is, therefore, called a *reducing agent.* Hydrogen will not reduce oxides of metals more active than iron. In every case, heating is necessary to cause the reaction to occur with noticeable speed.

Exercise

3. Write balanced equations for the reduction of the following oxides, assuming that the free metal is formed in every case: (*a*) Fe_3O_4, (*b*) Fe_2O_3, (*c*) PbO_2, (*d*) SnO, (*e*) Ag_2O.

Synthesis of Ammonia. Probably the most important chemical property of hydrogen, from an industrial point of view, is its ability (when under pressure and in the presence of suitable catalysts) to unite with the element nitrogen to form ammonia.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The perfecting of the processes for the large-scale production of ammonia by this method has had a most profound effect on whole nations. Nitrogen compounds, essential for fertilizers and explosives and formerly available in large quantities only through importation of saltpeter from Chile, can now be made anywhere in the world from the nitrogen of the air by using the above reaction.

Hydrogenation Processes. Hydrogen also has the property of uniting with the complicated compounds of carbon present in coal, crude oil, liquid vegetable oils or fats, and many related substances. Such reactions generally require the use of pressure and a suitable catalyst, and are called *hydrogenation processes.* The most commonly used catalyst is finely divided nickel.

5. Uses of Hydrogen. A survey of the properties of hydrogen immediately suggests its use for inflating balloons, for scientific experiments at very low temperatures, and for welding and similar processes requiring a high-temperature flame. However, the oxyacetylene flame is much more commonly used than the hydrogen flame, the latter being used only for special applications such as atomic-arc welding. As far as the amount of hydrogen used is concerned, all these uses are comparatively unimportant when compared with the use of hydrogen for the production of ammonia and for the hydrogenation of liquid vegetable oils to solid fats (Crisco), or the hydrogenation of low-grade coal and oil to produce gasolinelike liquids, in industrial regions where gasoline and crude oil are not abundant.

6. Industrial Methods for Producing Hydrogen. A common method is the water-gas process in which steam is allowed to react with carbon at a very high temperature (1000°C.). Often natural gas consisting chiefly of methane, CH_4, is substituted for carbon. The processes are represented by the following equations:

$$C + H_2O \rightarrow CO + H_2 \qquad \text{(water gas process)}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The CO and H_2 are usually separated by taking advantage of the fact that, under suitable conditions, the reaction

$$CO + \underset{\text{steam}}{H_2O} \rightarrow CO_2 + H_2$$

can be made to proceed nearly to completion. The carbon dioxide is highly soluble in water under pressure, and thus the hydrogen can be separated from the carbon dioxide.

Hydrogen is sometimes produced industrially by the electrolysis of water or brine solution, also by the reaction of steam with red-hot iron (see below), or, for military purposes, by the reaction of water with an iron silicon alloy.

7. Laboratory Preparation of Hydrogen. *Electrolysis of Water.* Hydrogen may be prepared from water by electrolysis if the water contains a small quantity of some acid, base, or salt to make it conduct electricity.

$$2H_2O \rightarrow 2H_2 + O_2$$

All of the hydrogen is liberated at the negative electrode (*cathode*) and all of the oxygen at the positive electrode (*anode*). The proportions by volume are always 2 volumes of hydrogen to 1 volume of oxygen.

Reaction of Metals with Cold Water. Only the most active metals react with cold water to produce hydrogen and a metallic hydroxide or base (V. 9). Examples:

$$2K + 2H_2O \rightarrow 2KOH + H_2$$
$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$
$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

A simple experiment for demonstrating the reaction of sodium with water can be done by making use of the apparatus shown in Fig. 2. A glass tube (1 by 20 cm.) is suspended in a 250-cc. beaker containing water. A small piece of sodium about 0.5 cm. in diameter, when dropped into the tube, reacts rapidly with the water. A lighted match placed at the upper end of the tube ignites the hydrogen, which burns with a yellow flame due to contamination by the sodium. A few drops of litmus solution or red litmus paper added to the water shows that a base (alkali) has been formed.

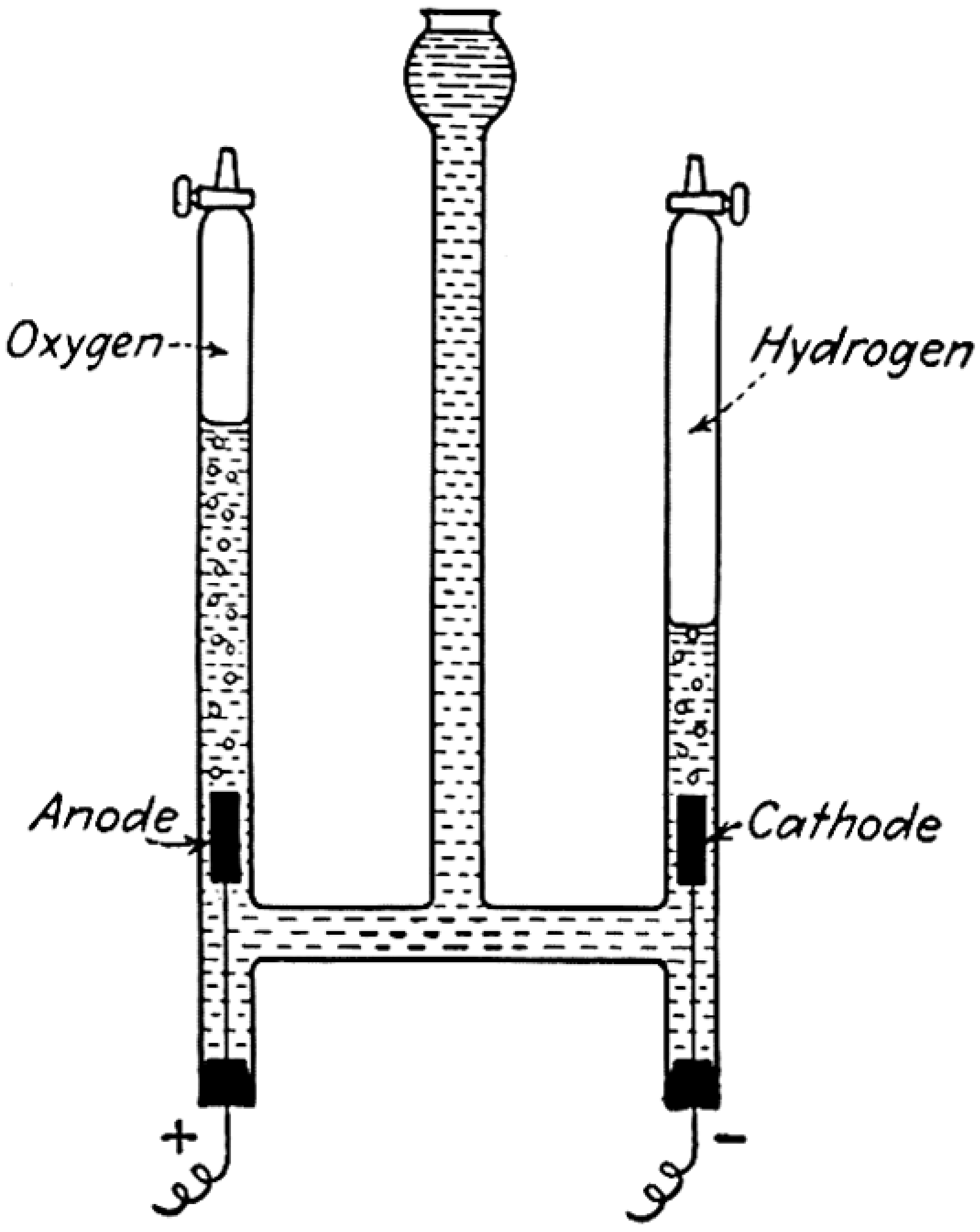

FIG. 1. Electrolysis of water.

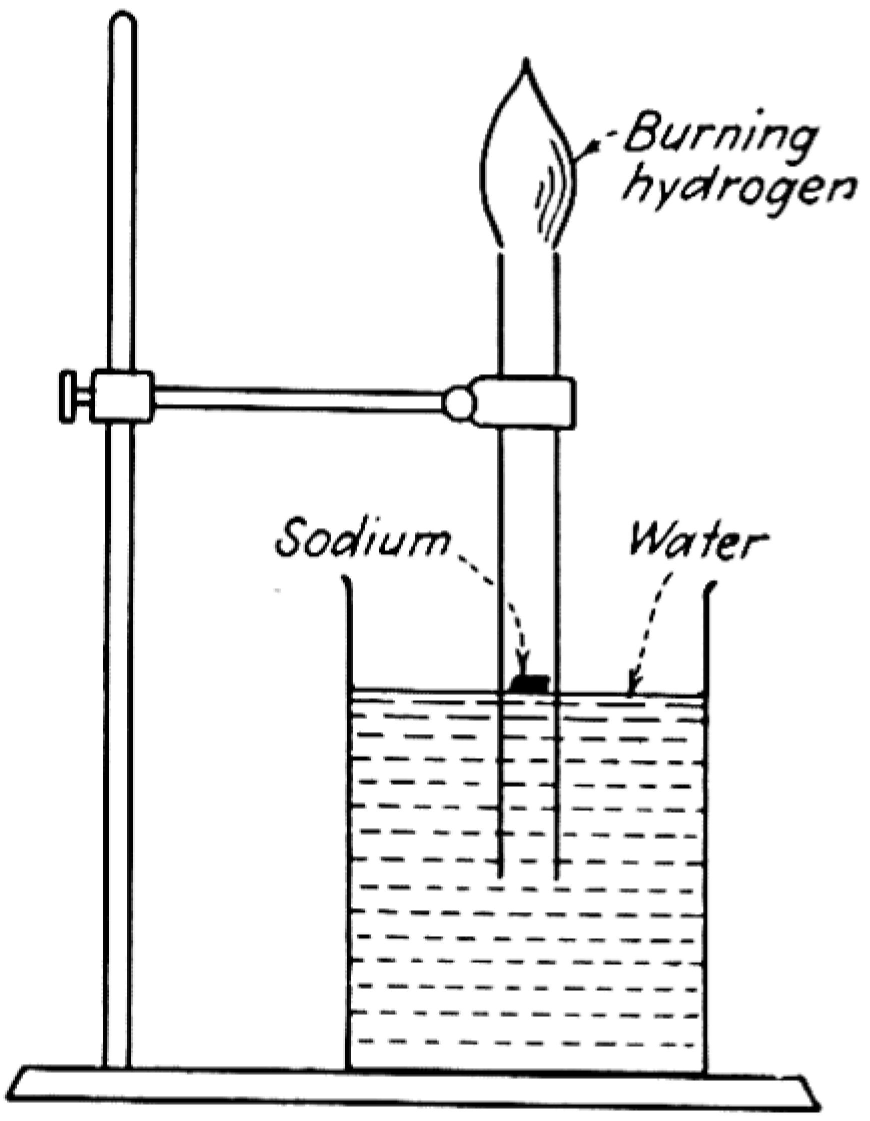

FIG. 2. Reaction of sodium with water.

Reaction of Metals with Steam. Some of the metals more active than hydrogen displace hydrogen from hot water or superheated steam. The other product is a metallic oxide. Examples:

$$Mg + H_2O \rightarrow MgO + H_2$$
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

The less the activity of the metal, the slower the reaction and the higher the temperature required. Metals less active than hydrogen do not react with water.

Reaction of Metals with Acids. All metals more active than hydrogen react with acid solutions, producing hydrogen and a salt (V. 9), the less active metals acting only very slowly. The speed of the reaction also varies with the acid used and with the state of subdivision of the metal. Examples:

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$
$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

The metals Zn, Fe, Al act similarly, giving $ZnSO_4$, $FeSO_4$, $Al_2(SO_4)_3$, $ZnCl_2$, $FeCl_2$, $AlCl_3$.

Exercise

4. Write balanced equations for the reaction of Zn, Fe, and Al (*a*) with HCl and (*b*) with H_2SO_4 (six equations in all).

Some acids, such as nitric acid, react with metals but ordinarily do not produce hydrogen.

Reaction of Metals with Bases. Zinc and aluminum react with strong solutions of sodium hydroxide or potassium hydroxide, producing hydrogen.

$$Zn + 2NaOH \rightarrow \underset{\text{sodium zincate}}{Na_2ZnO_2} + H_2$$

$$2Al + 2NaOH + 2H_2O \rightarrow \underset{\substack{\text{sodium}\\\text{metaaluminate}}}{2NaAlO_2} + 3H_2$$

8. Activity or Electromotive Series. The metals can be arranged in a series in decreasing order of their relative tendency to react with water and acids, displacing hydrogen, as follows:

K, Na, Ca, Mg, Al, Zn, Fe, Sn, Pb, H, Cu, Hg, Ag, Pt, Au
decreasing activity →

9. Bases, Acids, Salts. It has been shown in the preceding sections that active metals like sodium react with water, forming bases, and that less active metals like zinc react with acids, forming salts. We shall now examine a list of the more common bases, acids, and salts and learn the names of these compounds. (Review valence in Chap. III.)

Bases (Metal combined with the hydroxyl radical):

KOH	potassium hydroxide
$NaOH$	sodium hydroxide
$Ca(OH)_2$	calcium hydroxide
NH_4OH	ammonium hydroxide

Acids (Hydrogen combined with an acid radical):

HCl	hydrochloric acid
H_2SO_4	sulfuric acid
HNO_3	nitric acid
$HC_2H_3O_2$ (or $C_2H_4O_2$ or CH_3COOH)	acetic acid
H_3PO_4	phosphoric acid

Salts (Metal combined with an acid radical):

$ZnCl_2$	zinc chloride
$MgSO_4$	magnesium sulfate
$Ca(NO_3)_2$	calcium nitrate
$Zn(C_2H_3O_2)_2$	zinc acetate
Na_3PO_4	sodium phosphate

Exercise

5. Write the formulas of the sulfates of sodium, potassium, calcium, zinc, aluminum. Indicate the valence of each metal and radical.

10. Equivalent Weight. Definition. The equivalent weight of an element is the weight that will displace 1.008 g. hydrogen or combine with 35.45 g. chlorine. The term *equivalent weight* has numerous applications in chemical work and will be referred to in the study of normal solutions in Chap. VII.

A review of several reactions, with the atomic weights involved, will now be presented. (To simplify the relations, the hydrogen is expressed as atoms instead of molecules.)

$$\begin{array}{lcl} \mathrm{Na} + \mathrm{HCl} \rightarrow \mathrm{NaCl} + & & \mathrm{H} \\ 23\text{ g.} & & 1.008\text{ g.} \\ \mathrm{Zn} + 2\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + & & \mathrm{H, H} \\ 65.3\text{ g.} & & 2(1.008)\text{ g.} \\ \mathrm{Al} + 3\mathrm{HCl} \rightarrow \mathrm{AlCl_3} + & & \mathrm{H, H, H} \\ 27\text{ g.} & & 3(1.008)\text{ g.} \end{array}$$

From the definition of equivalent weight, it follows that

$$\frac{\text{Gram atomic weight of metal used}}{\text{Number of gram atomic weights of H displaced}} = \text{equivalent weight of the element}$$

Thus, the equivalent weights are as follows:

$$\frac{23\text{ g. Na}}{1} = 23\text{ g. sodium}$$

$$\frac{65.3\text{ g. Zn}}{2} = 32.6\text{ g. zinc}$$

$$\frac{27\text{ g. Al}}{3} = 9.0\text{ g. aluminum}$$

It is to be noted that the numbers, 1, 2, 3, are the respective valence numbers in the three compounds, $\overset{1+}{\mathrm{Na}}\mathrm{Cl}$, $\overset{2+}{\mathrm{Zn}}\mathrm{Cl_2}$, $\overset{3+}{\mathrm{Al}}\mathrm{Cl_3}$. These relationships can be summarized in the following statement: *The equivalent weight equals the atomic weight divided by the valence number.*

Exercises

6. Show the relation between the equivalent weight of the metal and the number of gram atomic weights of combined chlorine in the three chlorides shown above.

7. (*a*) Show that the equivalent weight of oxygen is 8 g. in H_2O, CaO, Al_2O_3, SiO_2, P_2O_5. (*b*) Calculate the equivalent weight of H, Ca, Al, Si, P, in these oxides. Refer to table of atomic weights (front cover).

11. Experimental Determination of Equivalent Weight. In laboratory work, it is desirable to determine the equivalent weight of a metal, *e.g.*, magnesium, by reaction with hydrochloric acid. Experimental data and calculations for an approximate determination, taken from a student's notebook, are presented below. The various steps should be carefully studied before beginning such an experiment.

Experimental Data:

Weight of metal used	0.1578 g.
Volume of hydrogen obtained	177 cc.
Temperature	19°C.
Barometric pressure	738 mm.
Vapor pressure of water	16.3 mm.
Corrected or true pressure	721.7 mm.

Results of Calculations from Experimental Data:

Volume of hydrogen at S.C.	157.1 cc.
Weight of hydrogen	0.014 g.
Equivalent weight of magnesium	11.36 g.
Error	0.8 g.
Percentage of experimental error	6.5%

Explanations of Calculations:

a. Correction of volume of hydrogen to standard conditions:

	Original	New
V	177 cc.	$V = ?$
T	19°C. 292°abs.	0°C. 273°abs.
P	721.7 mm.	760 mm.

$$V = 177 \times \frac{273}{292} \times \frac{721.7}{760} = 157.1 \text{ cc. } H_2 \text{ at S.C.}$$

b. Calculation of weight of hydrogen:

1,000 cc. or 1 l. H_2 at S.C. weighs 0.09 g.

$$157.1 \text{ cc. } H_2 \text{ at S.C. weighs } 157.1 \times \frac{0.09}{1{,}000} = 0.014 \text{ g.}$$

c. Calculation of equivalent weight of magnesium:

The experiment and calculations up to this point show that 0.014 g. H_2 was displaced by 0.1578 g. Mg, or that 1 g. H_2 would be displaced by 0.1578/0.014 g. Mg and that 1.008 g. H would be displaced by $1.008 \times \frac{0.1578}{0.014}$ g. Mg. Calculation of the last expression gives the value 11.36 g., which is the equivalent weight of magnesium according to this experiment.

d. Calculation of error and percentage of experimental error:

The error is the difference between the correct equivalent weight and the weight found by the experiment. The equivalent weight of magnesium, as determined with refined apparatus and all possible precautions, always comes out very close to 12.16, so this value is taken as the exact value. The percentage of experimental error is obtained as follows:

$$\%\text{ exp. error} = \frac{\text{error}}{\text{exact value}} \times 100 = \frac{0.8}{12.16} \times 100 = 6.5$$

NOTE: The average experimental error for several hundred determinations made by students using very simple apparatus was less than 5 per cent.

Exercises

8. The equivalent weight of a metal is 9. What weight of this metal will be needed to displace 3.024 g. H_2?

9. Calculate the equivalent weight of a metal if 0.27 g. of it displaces 175 cc. H_2 collected over water at 22°C. and 753 mm.

10. When 2.5 g. of a metal is dissolved in HCl, 857 cc. H_2 is evolved (measured over water at 18°C. and 775 mm.). Calculate the equivalent weight of the metal.

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CHAPTER VI

WATER

Water is the most important liquid known to man. Human, animal, and plant life cannot exist without water for very long and, for this reason, the provision of an adequate supply of it is a common problem in all countries. The human body contains about 70 per cent of water and many foods contain 75 per cent or more of water. The drying or dehydration of foods, therefore, is necessary when economy of shipping space and weight have to be considered. Milk powder, dried fruits, etc., are well known.

Numerous technical uses of water are familiar in engineering work, *e.g.*, in the production of steam for heat and power, as a medium for transmitting hydraulic pressure, and as a cooling medium in internal-combustion engines. In short, one may say that water is the great natural medium of life and energy.

1. Composition of Water by Volume. In the study of hydrogen (V. 7), it was shown that, when water is decomposed by an electric current (electrolysis), hydrogen and oxygen are set free in the proportion of exactly 2 volumes of hydrogen to 1 volume of oxygen. If hydrogen and oxygen are ignited by a spark in a closed glass tube over mercury and the tube is kept at a temperature above 100°C., it is always found that the relative volumes in the reaction are,

Hydrogen +	oxygen	forms	steam
2 vol. or	1 vol. or		2 vol. or
200 cc.	100 cc.		200 cc.

Any excess of hydrogen or of oxygen will be left uncombined in the tube. (Refer to Gay-Lussac's law, XIII.2.)

Exercise

1. If 50 cc. hydrogen and 100 cc. oxygen are mixed in a closed tube above 100°C. and ignited by a spark, what volumes of gases will be found in the tube?

2. Composition of Water by Weight. It is important for the student to learn that the composition of substances is determined by very careful experimental work, usually performed by a number of investigators. For example, Edward Morley, at Western Reserve

University, did extensive work on the composition of water. He burned hydrogen in oxygen and, by carefully weighing the hydrogen and the oxygen used and the water formed, he obtained the following data:[1]

Grams hydrogen used	3.7637
Grams oxygen used	29.8865
Grams water formed	33.6540

Exercise

2. From Morley's results (above), calculate (*a*) the percentage of hydrogen in water by weight, (*b*) the percentage of oxygen in water by weight, (*c*) the weight of hydrogen that combined with 8 g. oxygen, (*d*) the weight of hydrogen that combined with 16 g. oxygen. Derive the formula of water from the results in (*a*) and (*b*).

NOTE: The average combining ratio obtained by a number of investigators is 1.0078 g. hydrogen to 8 g. oxygen.

3. Purification of Water. Practically all natural water is impure in a chemical sense; however, it need not be chemically pure in order to be safe for drinking. It need only be free from harmful bacteria and poisonous substances. Other types of impurities are not dangerous to health. The impurities commonly present in natural water may be classified as follows:

a. Suspended matter of all kinds, generally clay, mud, leaves, etc.

b. Dissolved solids, which usually consist of mineral matter dissolved by water on passing through the ground. The hardness in water is due to this type of impurity.

c. Dissolved gases, almost always air.

d. Bacteria, which are included as a separate class because of their importance in connection with drinking water supplies. Bacteria may be found on particles of suspended matter.

Numerous methods are used for the purification of water. In some cases, these methods actually remove the impurities from the water, in other cases they destroy them by a chemical change. The more important methods are as follows:

a. Filtration, which removes suspended matter but not dissolved matter. Bacteria are never completely removed from water by filtration, although they may be removed in part by this process. It is desirable to use sedimentation or coagulation as a preliminary operation preceding filtration (Fig. 1).

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[1] *Am. Chem. J.*, 17, 267 (1895).

b. Sedimentation or *settling*, which removes the larger particles of suspended matter. Water-purification plants supplying water for cities have large settling basins.

c. Coagulation, which causes small particles of suspended matter to become attached to larger particles so that the rate of settling of all the particles is considerably increased. Coagulation is accomplished by adding lime and an aluminum or iron salt to the impure water. The lime forms calcium hydroxide, $Ca(OH)_2$, which reacts with the aluminum or iron salt to form a jellylike precipitate of aluminum hydroxide or iron hydroxide. These jellylike (gelatinous) precipitates have the property of causing coagulation.

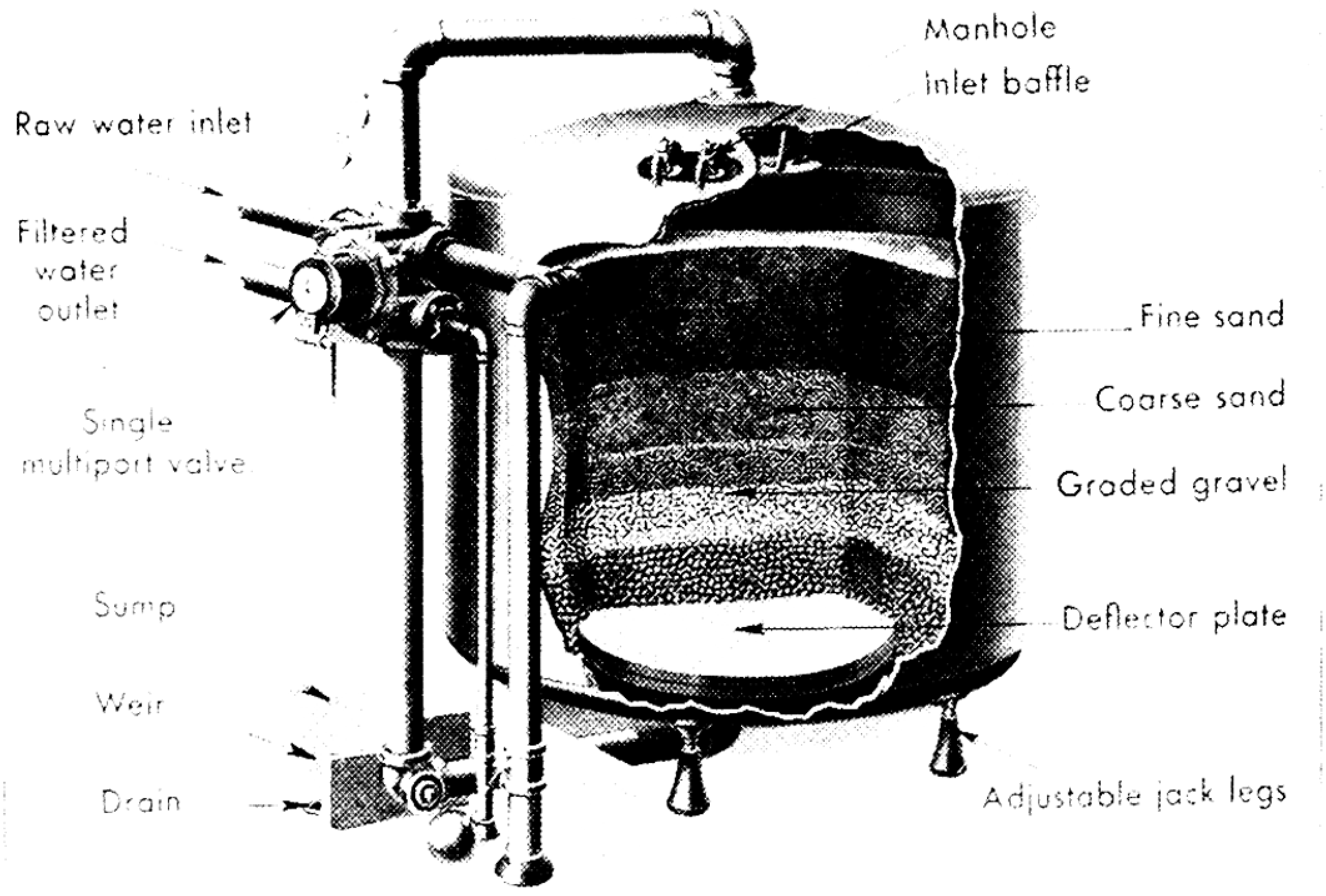

FIG. 1. Permutit Vertical Pressure Filter. (*Courtesy of the Permutit Company.*)

d. Boiling, which usually removes dissolved gases and destroys bacteria. However, not all gases are removed and complete destruction of bacteria sometimes requires boiling for a considerable time.

e. Distillation, which produces water free from nonvolatile impurities. Distilled water is used, for example, in storage batteries, because it contains no mineral salts which might interfere with the proper functioning of the battery.

f. Chemical treatment of many kinds, one of the most important of which is treatment with chlorine or a similar chemical (iodine, bleaching powder, potassium permanganate, etc.) that destroys bacteria but has no effect on most other types of impurities. A variation of this treatment is to spray the impure water into air, whereupon the oxygen destroys the bacteria. A different type of chemical treatment involves the addition of a water-softening substance such as lime, soda, or borax. These substances precipitate the soluble mineral salts, which can be removed by filtration. Reactions of this type are described in Chap. XXIX.

Filtration, sedimentation, and even distillation and chemical treatment take place regularly in nature. The production of rain water by evaporation and condensation is essentially distillation. Rain water is chemically pure except for dissolved air and possibly a slight trace of impurity derived from dust. Natural waters are slowly purified from harmful bacteria and organic matter, including sewage, by the action of the oxygen of the air.

Exercise

3. Name five common sources of natural water and suggest a suitable method for purification of the water from each source.

4. Vapor Pressure. Every liquid has a tendency to evaporate. The vapor formed in this way is really a gas and therefore exerts a gaseous pressure. If the liquid is in a closed container, this gaseous pressure rises only to a certain maximum value, depending upon the kind of liquid and the temperature. This maximum pressure is called the *vapor pressure* of the liquid for the particular temperature. The values for water are given in tables usually entitled *aqueous tension* or *vapor pressure of water* (see Appendix). No further evaporation takes place after the gaseous pressure of the vapor has attained the value of the vapor pressure. If the container is opened, some of the vapor will escape, the gaseous pressure of the remaining vapor will decrease to less than the vapor pressure, and evaporation will again take place. If compressed, some of the vapor will condense until its gaseous pressure is again equal to the vapor pressure, whereupon the condensation will stop.

Vapor pressure is thus a measure of the tendency of a liquid to evaporate. It may be defined as *the highest pressure that the vapor of a liquid can exert while it is in contact with the liquid at a given temperature.* Numerous solids also have a tendency to evaporate. The principles stated above can be applied in such cases. The vapor pressure is independent of the amount of liquid or solid present.

5. Vapor Pressure, Temperature, and Boiling Point. The vapor pressure of liquids always increases with temperature. The increase is slight at low temperatures, but becomes rapid at high temperatures. At certain temperatures the vapor pressure becomes equal to the total atmospheric pressure, and at this temperature the liquid boils. Thus the boiling point of a liquid is the temperature at which its vapor pressure equals or just exceeds the total pressure of the surrounding atmosphere. If the surrounding pressure is reduced, for instance, by placing some liquid in a bottle and pumping out some or all of the air in it, the liquid will boil at a temperature below its normal boiling point. On the other hand, if increased air pressure is applied to the surface of the liquid, its boiling point will be raised accordingly. It is important to realize that a given liquid has a different boiling point for each different pressure; when the pressure is fixed, the boiling point is also fixed. Application of more heat to a boiling liquid does not raise the temperature.

Exercises

4. What is the approximate vapor pressure of boiling water?
5. Is the temperature of boiling water always exactly 100°C. (212°F.)?
6. What pressure must exist in order for pure water to boil at exactly 100°C.? at 35°C.? at 30°C.?
7. Explain the operation of the vacuum evaporator used in the sugar-refining process, in terms of boiling point and vapor pressure.
8. Explain the operation of pressure cookers in terms of boiling point and vapor pressure.

6. Chemical Properties of Water. The reactions of water with metals, and with acidic and basic oxides, and the decomposition of water by electrolysis have already been studied.

Exercises

9. Write equations for the reaction of water or steam with (*a*) sodium, (*b*) potassium, (*c*) calcium, (*d*) magnesium, (*e*) iron.
10. Write equations for the reaction of water with two basic oxides and with three acidic oxides.

Water is not easily decomposed by heat. A temperature of 1000°C. produces no appreciable decomposition. Water combines with many salts to form hydrates.

7. Hydrates. If a solution of copper sulfate is allowed to evaporate until crystallization occurs, the crystals are found to have the composition $CuSO_4(H_2O)_5$. This formula is usually written $CuSO_4 \cdot 5H_2O$. Other common hydrates may be made in a similar manner and have compositions as follows: $ZnSO_4\cdot7H_2O$; $BaCl_2\cdot2H_2O$; $MgSO_4\cdot7H_2O$; $CaSO_4\cdot2H_2O$; and $Na_2CO_3\cdot10H_2O$. A hydrate is a compound formed by the union of water with a salt and from which water is easily removed by heat. Some hydrates are liquids, but most common ones are solids. It will be noted that the number of molecules of water united with a molecule of salt varies in an irregular manner and that ordinary rules of valence are of no use in attempting to work out the correct formula for a hydrate. The water that is combined with the salt is called *water of crystallization* or *water of hydration.* A salt without water of crystallization is referred to as an *anhydrous salt.* An equation for the formation of a hydrate is written:

$$CuSO_4 + 5H_2O \rightleftarrows CuSO_4\cdot5H_2O$$

The effect of heat on a hydrate may be expressed by the reverse of the equation just given. The loss of water from a hydrate or other substance is known as *dehydration.* A practical illustration of the reversible process of dehydration-hydration is the formation of plaster of paris from gypsum by dehydration and the subsequent hardening of the plaster by hydration. Plaster of paris is widely used for making surgical casts for broken bones and for the formation of interior decorative forms. The equation for this reaction is as follows:

$$\underset{\text{gypsum}}{2(CaSO_4\cdot2H_2O)} \underset{\text{hydration}}{\overset{\text{dehydration}}{\rightleftarrows}} \underset{\text{plaster of paris}}{(CaSO_4)_2\cdot H_2O} + 3H_2O$$

Exercises

11. Write equations for the effect of heat on each of the hydrates whose formulas are given in the preceding paragraph.

12. Show how to calculate the percentage of water in two of the above hydrates.

13. Show how to calculate the percentage of water lost in the formation of plaster of paris from gypsum.

The number of moles of water per mole of salt in a hydrate is determined in the laboratory by the following method. A known weight of the pure hydrate is heated to constant weight in a crucible. The loss in weight (weight of water) is divided by the molecular weight of water. The weight of the residue (weight of anhydrous salt) is divided by the molecular weight of the anhydrous salt. These two quotients reduced to lowest terms indicate the relative number of moles of water per mole of anhydrous salt. This method is based upon two assumptions: (1) that all of the water is driven off by heat and (2) that the anhydrous salt is not decomposed by heat.

Exercise

14. When 2.77 g. of a hydrate of barium chloride was heated to constant weight in a crucible, there was a loss in weight of 0.42 g. (of water). Derive the formula of the hydrate from these data. Show all calculations.

8. Efflorescence. Efflorescence is *the loss of water from a hydrate into the surrounding atmosphere at ordinary temperature and pressure.* Not all hydrates undergo efflorescence. The water of crystallization of a hydrate has a definite tendency to escape from the crystalline hydrate into the surrounding atmosphere. This tendency of the water of crystallization to evaporate is measured by the vapor pressure of the hydrate. Some hydrates have relatively large, and others very small, vapor pressures. A hydrate will effloresce only if its vapor pressure is greater than the pressure of the water vapor in the surrounding air. An anhydrous salt will spontaneously take on water from the air if the hydrate formed has a vapor pressure lower than the pressure of the water vapor in the surrounding air. The vapor pressure of a hydrate is analogous to the vapor pressure of liquid water.

9. Deliquescence. Deliquescence is *the absorption of water by a substance from the surrounding atmosphere.* It may be regarded as the reverse of efflorescence. Salts that are very soluble in water, *e.g.*, calcium chloride, exhibit this property. The salt tends to dissolve in the absorbed water and form a saturated solution, the vapor pressure of which is lower than the vapor pressure of the water vapor in the surrounding atmosphere. Practical use of this property is found in the application of calcium chloride to dirt roads to prevent dust formation.

10. Reversible Changes and Equilibrium. The evaporation and condensation of water provide an example of a reversible physical change. A reversible change is one that may take place in both the forward and the reverse direction. In the case of the evaporation and condensation of water, both changes are always going on at the same time. The explanation for this arises from the kinetic molecular hypothesis. Any sample of liquid water is continuously losing some of its more rapidly moving molecules to the surrounding atmosphere, and is also continuously regaining water molecules from the atmosphere. If the number of molecules leaving the liquid is greater than the number returning, the process is called *evaporation* because the condensation cannot be observed. If the number of molecules returning to the liquid is greater, the process is called *condensation* because the evaporation cannot be observed. If the number of molecules returning equals the number leaving, neither evaporation nor condensation can be observed and a state of equilibrium exists. This is the situation within a stoppered bottle partly filled with water. Both evaporation and condensation are going on, but neither process can be observed because the two opposing changes are going on at equal rates. The three cases may be represented by diagrams (Fig. 2).

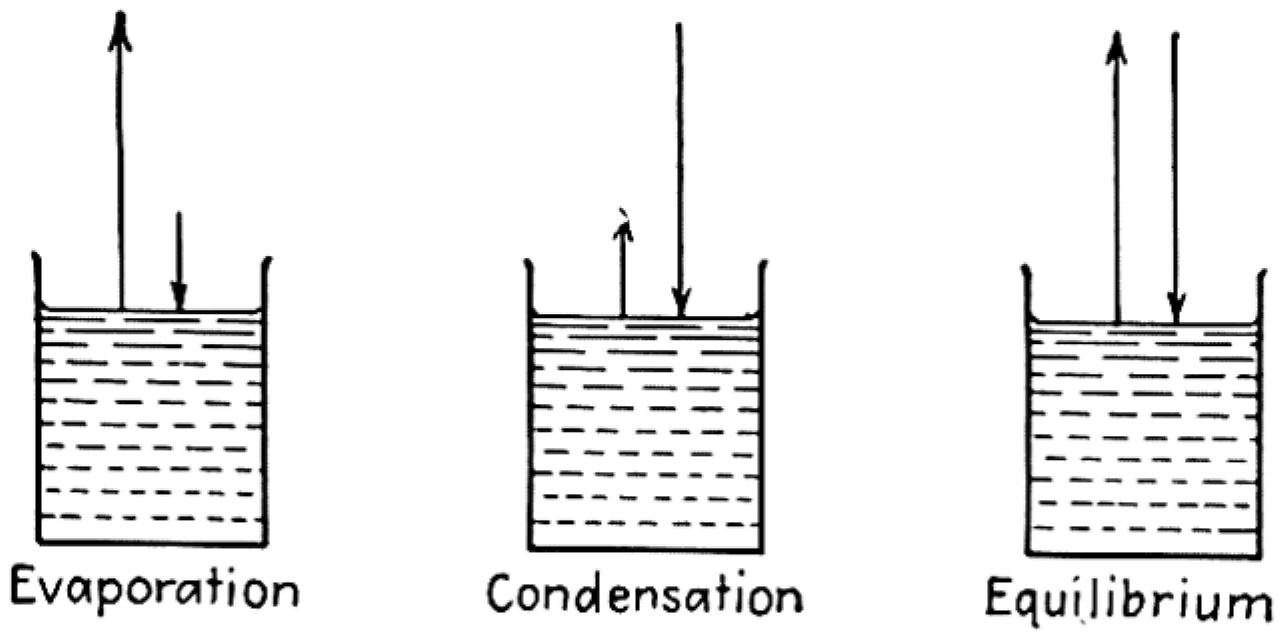

FIG. 2. Evaporation-condensation equilibrium.

The formation and decomposition of a hydrate provide an example of a reversible chemical reaction (VIII, 2), and may be represented by an equation with double arrows, as follows:[1]

$$CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 + 5H_2O$$

Obviously, the effect of heat must be greatly to increase the rate of the forward action, so that it alone is noticeable. When the amount of moisture in the air (pressure of water vapor in air) is relatively small, the reverse reaction (←) is necessarily slow and only the forward reaction is observed, *i.e.*, the hydrate undergoes efflorescence. If the air is moist or if the forward reaction is limited, the situation will be reversed. If the hydrate is kept in a closed bottle, a state of equilibrium will soon be reached.

11. Characteristics of Equilibrium. Equilibrium is characterized by

a. Two opposing processes.

b. Equal rates for the two opposing processes so that no net change is observable.

c. A slight change in condition disturbs the equilibrium because the change increases or decreases the rate of one process more than the other.

Exercises

15. What are the two changes going on at equal rates in a stoppered bottle partly full of water?

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[1] Other hydrates, $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$ are formed at definite vapor pressures.

16. Under what condition will water fail to evaporate from an open vessel?

17. Explain in terms of vapor pressure why water usually evaporates completely from an open vessel but not from a closed vessel. Give the same explanation in terms of the kinetic theory.

18. What would happen to a small piece of ice if kept in a very large stoppered bottle of dry air at 0°C.?

19. What determines the loss of moisture from foods stored in a refrigerator? How can this loss be decreased?

20. Explain why blue vitriol, $CuSO_4 \cdot 5H_2O$, sometimes appears white. How could this color change be prevented? (Refer to laboratory work.)

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CHAPTER VII

SOLUTIONS

Ocean water contains about 3 per cent dissolved salts, principally sodium chloride, and may be regarded as the best known example of a solution. The properties of solutions are of great interest and importance both in theoretical and in applied chemistry. When we add a small amount of ordinary table salt, NaCl, to a glass of water, we observe that the salt tends to disappear or dissolve in the water, that no salt settles out of the solution, and that variable amounts of salt can be dissolved in the water.

1. Definition and Characteristics of a True Solution. *A true solution is a homogeneous mixture of two or more substances* and has the following characteristics: (1) spontaneous formation, (2) subdivision down to molecular magnitudes, (3) absence of settling, (4) no fixed proportions of the substances used, as in the case of a compound.

2. Types of Solutions. Solutions may be formed by dissolving a solid in a liquid, one liquid in another (alcohol in water), a gas in a liquid (Coca-Cola), one gas in another (air), a gas in a solid, a liquid or solid in another solid. The first four types are the most common.

3. Difference between Dissolving and Melting. The dissolving of a solid in a liquid should not be confused with the melting of a solid. In both cases, a solid disappears into a liquid. In melting, the solid and the liquid are the same substance; in dissolving, the liquid and the solid are different substances. Application of heat is essential to form the liquid in melting; heat is involved to a lesser extent in dissolving a solid in a liquid.

4. Solute and Solvent. In the cases of solids or gases dissolved in liquids, the liquid is called the solvent and the solid or gas (the dissolved substance) is called the *solute.*

5. Solutions and the Kinetic Theory. Whenever a solution is in contact with an excess of solute, two opposite processes (dissolving and crystallizing) are continuously going on. This means that solute molecules are (1) leaving the crystal and going into the solution (dissolving) and (2) returning from the solution to be deposited on the crystal (crystallization).

6. Saturated Solution. *A saturated solution may be defined as one of such strength that, when placed in contact with an excess of solute, it is in equilibrium.* In this case, crystallization and dissolving are taking place at the same rate; *i.e.*, the same number of molecules leave and return to the solid in any period of time. This is obviously a case of equilibrium.

An *unsaturated solution* is one that is less concentrated (weaker) than the saturated solution at the same temperature; a *supersaturated solution* is more concentrated (stronger) than the saturated solution of the same substance at the same temperature. If the solution is unsaturated, dissolving is more rapid than crystallization; *i.e.*, more molecules are leaving the crystal than are returning to it. If the solution is supersaturated, crystallization is more rapid than dissolving, *i.e.*, more molecules deposit on the crystal than dissolve from it. These three types of solutions may be distinguished from one another by addition of a crystal of solute. In the case of the unsaturated solution, the added crystal will dissolve; in the case of the saturated solution, the added crystal will remain unchanged; in the case of the supersaturated solution, more crystals will form around the original added crystal.

7. Solubility and Insolubility. There is a maximum amount of solute that can be dissolved at a given temperature in a given amount of solvent by mixing the two and shaking the mixture. This maximum is called the *solubility*. Thus, not more than 35.86 g. common salt can be dissolved in 100 g. water at ordinary temperature (18°C) by shaking solid salt with water. The solubility of common salt is said to be 35.86 g. per 100 g. water at 18°C.

Similarly, as much as 0.00013 g. silver chloride $AgCl$, can be dissolved in 100 g. water at ordinary temperature (18°C.). So the solubility of $AgCl$ is said to be 0.00013 g. per 100 g. water. When the solubility of a substance is very low, it is often spoken of as *insoluble.* Actually, of course, it is very slightly soluble. Solutions such as those mentioned above are of course saturated solutions since, after thorough shaking of solute and solvent, equilibrium must be established.

Exercises

1. From the solubility table in the Appendix, list the formulas of five other insoluble salts.

2. Find the solubility at 18°C. of each of the following: $NaOH$, Na_2CO_3, $CaCl_2$, $MgSO_4$, $ZnCO_3$.

NOTE: At this point the instructor may prefer to take up Secs. 17 to 21 ("Methods of Expressing Concentration of Solutions").

8. Temperature and the Solubility of Solids in Liquids. Increase in temperature usually increases the solubility of a solid in a liquid. (Increase in pressure has negligible effect.) The variation of solubility with temperature may be shown by a *solubility curve*, which is a line drawn through the solubility values at various temperatures, when plotted on a graph. The solubility values have to be experimentally determined. The solubility curves for some common substances are shown in Fig. 1.

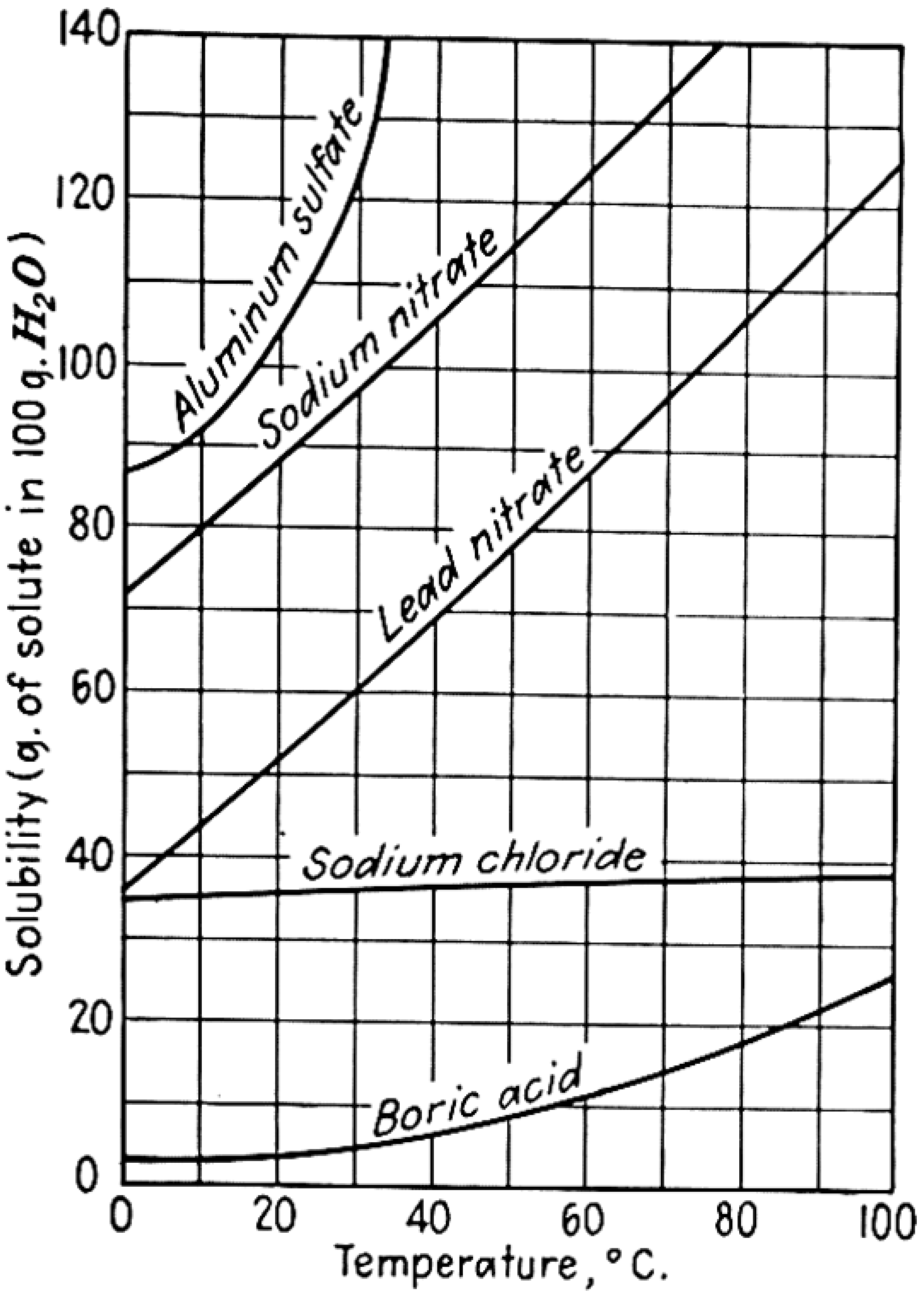


FIG. 1. Solubility-temperature curves.

Exercises

3. From the curves in Fig. 1, prepare a table showing the solubilities of (*a*) sodium chloride, (*b*) sodium nitrate, at 20, 40, 60, 70°C. in 100 g. water.

4. Would it be a distinct advantage to use boiling water to dissolve salt, NaCl, in salt wells? Calculate the percentage increase in the solubility of NaCl between the temperatures 0 and 100°C.

9. Supersaturated Solutions. A supersaturated solution is obtained by preparing a saturated solution at some elevated temperature and then carefully cooling this solution in the absence of solid solute. In many cases, crystallization will occur on cooling, and the result is merely a saturated solution. In a few cases, crystallization will fail to occur during cooling, and thus a solution is obtained that is more concentrated than the saturated solution at room temperature. Such a supersaturated solution is unstable since the addition of solid solute causes crystallization to begin and continue until a saturated solution is obtained. In fact, crystallization of a supersaturated solution often occurs on mere shaking or stirring, or on the entry of dust particles. A supersaturated solution may also be prepared by mixing two solutions that react to produce a slightly soluble substance. Usually this substance will appear immediately as a precipitate, but in some cases it fails to do so and a supersaturated solution is formed.

Exercise

5. Small portions of KI and $Pb(NO_3)_2$ solutions are mixed so that the following reaction occurs:

$$2KI + Pb(NO_3)_2 \rightarrow \underset{\text{Lead iodide}}{PbI_2} + 2KNO_3$$

The KNO_3 is very soluble and remains entirely in solution, but the PbI_2 is only slightly soluble and so cannot remain entirely in solution. The excess appears as a precipitate of yellow lead iodide, PbI_2. Indicate whether each of the following is a saturated, unsaturated, or supersaturated solution:

a. The clear liquid after the excess PbI_2 has settled to the bottom.

b. The liquid obtained upon heating after the excess PbI_2 has dissolved.

c. The perfectly clear liquid obtained by carefully cooling *b* to room temperature.

10. Effect of Temperature and Pressure on the Solubility of Gases in Liquids. Increase in temperature usually decreases the solubility of a gas in a liquid, while increase in pressure increases the solubility of a gas in a liquid. *The weight of a gas dissolved in water varies directly with the pressure* (Henry's law).

Exercises

6. If 3 mg. nitrogen dissolve in 1 l. water at a certain temperature, under a pressure of 1,140 mm. mercury, how much will dissolve at the same temperature in 100 cc. water, under a pressure of 15 atm.?

7. Use the kinetic theory to explain the effect of (*a*) temperature and (*b*) pressure on the solubility of gases in liquids.

11. Simple Dissolving. Simple dissolving is any case of dissolving that takes place without chemical action; *e.g.*, the dissolving of sugar in water. Chemical dissolving is any case of dissolving that takes place with chemical action; *e.g.*, zinc dissolving in sulfuric acid.

12. Miscible Liquids, Immiscible Liquids, Emulsions. *Miscible liquids* are liquids that will dissolve in one another; *immiscible liquids* will not dissolve in one another but form separate layers. If two immiscible liquids are shaken together, they will mix and form an emulsion. An *emulsion* is a mixture of one finely divided liquid with another liquid. Most emulsions separate immediately into layers when shaking is stopped, but in the presence of a properly chosen third substance (a stabilizer) some emulsions become stable and then may not separate into layers for a long period of time.

13. Law of Partition or Distribution. A solute distributes itself between two immiscible liquids in proportion to its solubility in each liquid alone.

14. Suspensions. A suspension is a mixture of a finely divided solid with a liquid. Solutions, suspensions, and colloidal suspensions differ in the size of the suspended particles. In true solutions, these particles are the molecules (or ions) of the solute. In the suspension, they are particles of the suspended material. In the colloidal suspension, they are also particles of the suspended material but are so small that the colloidal suspension does not settle, appears homogeneous to the eye, and will readily pass through filter paper.

15. Freezing Points of Solutions. The freezing point of a solution is always lower than the freezing point of the corresponding pure solvent. In general, the lowering of the freezing point becomes more marked as the concentration of the solution is increased. Application is made of this fact by adding substances such as alcohol to automobile radiator liquids during cold weather. The lowering of the freezing point of a solution depends upon the number of moles of alcohol or glycerin, for example, that are added to 1,000 g. water, as indicated by Table I.

TABLE I

Substance	1 mole	Freezing point of solution
Alcohol, C_2H_5OH	46 g.	−1.86°C.
Glycerin, $C_3H_5(OH)_3$	92 g.	−1.86°C.
Ethylene glycol, or Prestone, $C_2H_4(OH)_2$	62 g.	−1.86°C.

Assuming a direct proportionality between the number of moles of solute added and the lowering of the freezing point (not strictly true for higher concentrations), it follows that the addition of 2 moles of alcohol (2 × 46 g.) to 1,000 g. water would form a solution that would freeze at 2 × (−1.86°C.) or −3.72°C.

Exercise

8. What weight of pure glycerin would have to be added to 1,000 g. water to form a solution that would not freeze above −1°F.?

It is advisable, of course, to follow the standard specifications provided on charts at garages in preparing antifreeze solutions because of the fact that the antifreeze preparations are not usually single compounds but often contain other materials, such as rust inhibitors or water. Furthermore, it is not advisable to add inorganic substances, *e.g.*, calcium chloride, because of their corrosive effects in the cooling systems. The addition of such compounds to water lowers the freezing points to a greater extent than do substances like alcohol and glycerin, at the same molar concentration.

16. Boiling Points and Vapor Pressure of Solutions. The vapor pressure of a solution of a nonvolatile solute, *e.g.*, sugar, in a liquid is less than the vapor pressure of the liquid at the same temperature. The boiling point of such a solution is always higher than that of the pure liquid. The lowering of the vapor pressure and the rise in the boiling point become greater as the concentration increases. A nonvolatile solute is one that has no tendency to vaporize or evaporate; *i.e.*, it has no appreciable vapor pressure. Salt and sugar are examples of nonvolatile substances.

17. Methods of Expressing Concentration of Solutions. A *dilute* (weak) *solution* is one containing a small proportion of dissolved material (solute); a *concentrated* (strong) *solution* is one containing a large proportion of dissolved material. A 10 per cent solution contains 10 g. solute and 90 g. solvent in 100 g. solution; a 15 per cent solution contains 15 g. solute and 85 g. solvent, etc.

Chemists generally use either the *normal* or the *molar* system of expressing the concentration or strength of solutions. The normal system requires the use of the equivalent weights of acids, bases, and salts. The molar system uses molecular weights.

TABLE II

Compound	Molecular weight	Total valence of positive radical	Equivalent weight
H_2SO_4	98	2	49
HCl	36.5		
H_3PO_4	98		
$NaOH$	40		
$Ca(OH)_2$	74		
$CuSO_4$	159.6		
$CuSO_4 \cdot 5H_2O$	219.6	2	
$Al_2(SO_4)_3$	342	..	57
Na_2SO_4	142	..	71

18. Equivalent Weights of Acids, Bases, and Salts. In general, the *equivalent weight* of any substance is that weight which contains, or is equivalent to, one atomic weight of hydrogen. The equivalent weight of any acid, base, or salt equals the molecular weight divided by the total valence of the positive radical, as illustrated in Table II. In computing total valence of a hydrate, the water of hydration is not considered.

Exercise

9. Copy Table II and fill in the data not calculated.

19. Normal Solutions. A *normal* (1*N*) *solution contains* 1 *equivalent weight of solute per liter of solution.* A two normal (2*N*) solution contains 2 equivalent weights of solute per liter of solution; a 2.6*N* solution contains 2.6 equivalent weights of solute per liter of solution, etc.

20. Problems on Normal Solutions.

Example 1. Calculate the weight of H_2SO_4 needed to make, or that is present in, 3 l. of 0.5*N* solution.

Answer: $49 \times 3/1 \times 0.5 = 73.5$ g. H_2SO_4

In this example, 49 represents the equivalent weight of sulfuric acid, *i.e.*, the weight needed to make 1 l. of 1*N* solution. This value must be multiplied by 3, because the problem calls for 3 l. of solution, and also by 0.5, because the problem calls for a 0.5*N* solution.

Example 2. Calculate the weight of $CuSO_4$ found in 25 cc. of 6*N* solution.

Answer: $79.8 \times \frac{25}{1{,}000} \times 6 = 11.97$ g.

It is necessary to convert the cubic centimeters to liters (1 cc. = 1/1,000 l.; 25 cc. = 25/1,000 l.) before proceeding with the solution of the problem.

Example 3. A solution is found to contain 8 g. Na_2SO_4 in 320 cc. What is the normality of this solution?

Answer: In the above solution,

320 cc. contains 8 g. Na_2SO_4.

1 cc. contains $8/320$ g. Na_2SO_4.

1,000 cc. or 1 l. would contain $1{,}000 \times 8/320$ g. Na_2SO_4.

The exact normality is given by the ratio:

$$\text{Normality} = \frac{\text{actual weight per liter}}{\text{equivalent weight}} = \frac{25}{71} = 0.35N$$

Exercises

10. Find the weight of H_2SO_4 present in 8.5 l. of 6*N* solution.
11. Find the weight of $Ca(OH)_2$ necessary to make 5 l. of 0.1*N* solution.
12. Find the weight of $CuSO_4 \cdot 5H_2O$ required to make 500 cc. of 2.5*N* solution.

21. Molar Solutions. A *molar* (1M) *solution contains* one *molecular weight of solute per liter of solution;* a 2M solution two molecular weights, etc. It will be observed that the *molar system is based on molecular weights and the normal system on equivalent weights.*

Exercises

13. Calculate the weight of $CuSO_4$ required for each of the following: (*a*) 1 l. of 1M solution, (*b*) 12 l. of 7.3M solution.

14. Calculate (*a*) the molar concentration of a solution containing 34.2 $Al_2(SO_4)_3$ per liter of solution, (*b*) the normal concentration of this solution (see Example 3 above).

CHAPTER VIII

HYDROGEN CHLORIDE AND SODIUM HYDROXIDE

Hydrochloric acid is a water solution of the gas, hydrogen chloride, HCl. It is a well-known acid. Sodium hydroxide, $NaOH$, dissolved in water is a common base or alkali. These compounds are used extensively, both in the laboratory and in industry. They are generally made from sodium chloride, $NaCl$, or common salt.

1. Preparation of HCl. In general, HCl may be prepared by the reaction of almost any metallic chloride with concentrated sulfuric acid as illustrated by the following equations:

$NaCl + H_2SO_4 \rightarrow HCl\uparrow + NaHSO_4$ (sodium bisulfate)
$KCl + H_2SO_4 \rightarrow HCl\uparrow + KHSO_4$ (potassium bisulfate)
$NH_4Cl + H_2SO_4 \rightarrow HCl\uparrow + NH_4HSO_4$ (ammonium bisulfate)
$CaCl_2 + H_2SO_4 \rightarrow 2HCl\uparrow + CaSO_4$ (normal calcium sulfate)
$2AlCl_3 + 3H_2SO_4 \rightarrow 6HCl\uparrow + Al_2(SO_4)_3$ (normal aluminum sulfate)

The arrow pointing upward indicates an escaping gas. Such an arrow is generally used in cases of this kind.

It is to be noted that only $NaCl$, KCl, and NH_4Cl produce bisulfates; all other chlorides produce normal sulfates when they react with sulfuric acid. The chlorides of Na, K, and NH_4 give normal sulfates only when the reactions occur at high temperatures. Bisulfates contain the HSO_4 radical (valence -1); normal sulfates contain the SO_4 radical.

Exercise

1. Write equations for the reactions of H_2SO_4 with chlorides of five different metals other than those given above.

In the laboratory, HCl is generally prepared by the reaction of solid $NaCl$ with concentrated H_2SO_4 as indicated in the first of the above equations. This same method is also used in industry. The $NaCl$ is also mixed with sodium bisulfate and the mixture heated.

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl\uparrow$$

Other industrial methods are illustrated by the following equations:

$$H_2 + Cl_2 \rightarrow 2HCl$$
$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$

(C_5H_{12} is called *pentane* and is a material obtained chiefly from natural gas.)

2. Reversible Chemical Reactions. At least two examples of reversible physical processes (evaporation and condensation of water; dissolving and crystallizing of a solute) have already been considered, and the characteristics of equilibrium in such cases have been stated (VI. 11). *A reversible chemical reaction is one that will take place in either or both of the two possible directions.* A large number of chemical reactions (VI. 7, VIII. 2) are reversible and reach an equilibrium with characteristics similar to those previously mentioned. Another example of a reversible reaction is the following:

$$NaCl + H_2SO_4 \rightleftarrows HCl + NaHSO_4$$

in which the double arrows indicate the reversible nature of the reaction.

3. Direction of a Reversible Reaction, Chemical Equilibrium. The reaction

$$NaCl + H_2SO_4 \rightleftarrows HCl + NaHSO_4$$

will proceed to completion in the forward direction (to the right) if solid sodium chloride and concentrated sulfuric acid are mixed, because HCl escapes as a gas under these circumstances, and the reverse reaction is impossible without HCl.

Forward direction:

$$\overset{\text{solid}}{NaCl} + \overset{\text{conc.}}{H_2SO_4} \rightarrow \overset{\text{gas}}{HCl\uparrow} + NaHSO_4$$

The reaction will proceed toward completion in the reverse direction (to the left) if concentrated hydrochloric acid and concentrated solution of sodium hydrogen sulfate are mixed, because NaCl is removed from the reaction as a precipitate.

Reverse direction:

$$\overset{\text{conc.}}{HCl} + \overset{\text{saturated}}{NaHSO_4} \rightarrow \underset{\text{precipitate}}{NaCl\downarrow} + H_2SO_4$$

If more than a minimum quantity of water is present, both HCl and NaCl will remain in the solution and both reactions will occur simultaneously. They will soon become equal in rate, and chemical equilibrium will thus be reached. In this case, the reaction will be incomplete since the starting materials are continuously regenerated by the reverse reaction as rapidly as the forward reaction consumes them.

It is to be observed that the characteristics of chemical equilibrium are essentially the same as those mentioned for physical equilibrium (VI. 11):

a. Two opposing processes, *i.e.*, the forward and the reverse reactions.

b. Equal speeds for these two processes.

c. A slight change disturbs the equilibrium; *i.e.*, addition of a further quantity of any one of the materials used or produced favors either the forward or the reverse reaction.

In general, in any reversible reaction the conditions favoring equilibrium are as follows:

a. Failure of any substance to be removed from the reacting mixture.

b. Low concentration of starting materials.

The conditions favoring complete reaction are as follows:

a. Removal of one or more products from the mixture as a gas or a precipitate.

b. High concentration of starting materials.

There is a useful analogy (to a limited extent) between the direction of a reversible reaction and the direction of flow of water in a pipe between two containers of liquid as shown in Fig. 1.

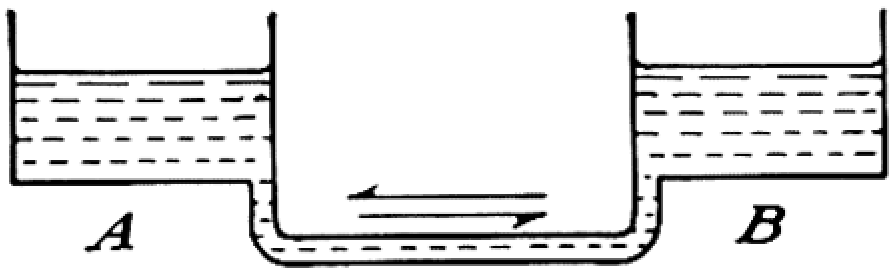


FIG. 1. Hydraulic analogy of equilibrium.

$$NaCl + H_2SO_4 \rightleftarrows HCl + NaHSO_4$$

The increase in concentration of NaCl or H_2SO_4 results in an effect in the same direction as an increase in the amount of liquid in *A*. Removal of liquid from *B* results in an effect in the same direction as the removal of HCl or $NaHSO_4$ from the chemical mixture.

It is important to realize that the chemical equilibrium is a dynamic one (both the forward and the reverse changes are in full operation at equilibrium) while the fluid equilibrium is a static one (no flow at all, at equilibrium).

Exercise

2. Which of the following reactions is complete, which incomplete, taking into account that AgCl is the only insoluble substance among those included in the two equations?

$$HCl + AgNO_3 \qquad AgCl + HNO_3$$
$$HCl + KNO_3 \qquad KCl + HNO_3$$

Insert double or single arrows to indicate your answer.

4. Hydrogen Chloride, HCl, and Hydrochloric Acid, HCl. It is of importance to distinguish between the pure gas HCl (hydrogen chloride) and the water solution of this gas (hydrochloric acid or muriatic acid). Note that the same formula is used for both and that the context determines whether HCl refers to the gas or the acid. (For calculations involving specific gravity, see VIII. 8.)

5. Chemical Properties of Pure HCl Gas. These may be summarized by the statement that it is rather inactive and has almost none of the properties of an acid. It does unite with ammonia, NH_3, to form ammonium chloride, and with H_2O to form hydronium chloride.

$$NH_3 + HCl \rightarrow NH_4Cl$$
$$H_2O + HCl \rightarrow H_3OCl$$

The radicals of H_3OCl are H_3O and Cl, and it is probably the presence of the H_3O radical (or ion) in hydrochloric acid that makes it behave so very differently from pure HCl. However, the formula H_3OCl is seldom used for hydrochloric acid.

6. Chemical Properties of Hydrochloric Acid. These may be illustrated by its reaction with metals, its reaction with bases and basic oxides, forming salts and water (neutralization), and its reaction with silver nitrate and with ammonia.

Exercises

3. Write equations for the reactions of HCl with five different metals.

4. Write equations for the reactions of HCl with each of the following bases:

(*a*) $NaOH + HCl \rightarrow NaCl + H_2O$
(*b*) $Ca(OH)_2 + ?HCl \rightarrow CaCl_2 + ?H_2O$
(*c*) $Al(OH)_3 + ?HCl \rightarrow$
(*d*) KOH
(*e*) NH_4OH
(*f*) $Mg(OH)_2$
(*g*) $Cu(OH)_2$
(*h*) $Fe(OH)_3$

5. Write equations for the reaction of HCl with each of the following basic oxides: (*a*) CaO, (*b*) MgO, (*c*) ZnO, (*d*) Al_2O_3, (*e*) Fe_2O_3. *Example*, $CaO + 2HCl \rightarrow CaCl_2 + H_2O$.

6. Write equations for the reaction of HCl (*a*) with silver nitrate, (*b*) with ammonia.

7. Tests for HCl. HCl gas fumes in moist air, forms a white cloud of NH_4Cl when brought into contact with ammonia gas, and dissolves in water very rapidly forming hydrochloric acid. The latter can be detected by its effect on indicators (litmus, phenolphthalein, methyl orange) and by its reaction with silver nitrate and with bases.

8. Specific Gravity and Concentration of Hydrochloric Acid. It is often necessary in chemical work to know the exact quantity (concentration) of hydrogen chloride dissolved in a given amount of solution. We can determine the specific gravity of a sample of the acid by means of a hydrometer similar in principle to the type used in garages for measuring the specific gravity of sulfuric acid. The hydrometer is immersed in the acid which is placed in a tall narrow cylinder (Fig. 2). Tables showing the percentage by weight of hydrogen chloride corresponding to a given specific gravity are found in laboratory manuals and handbooks.

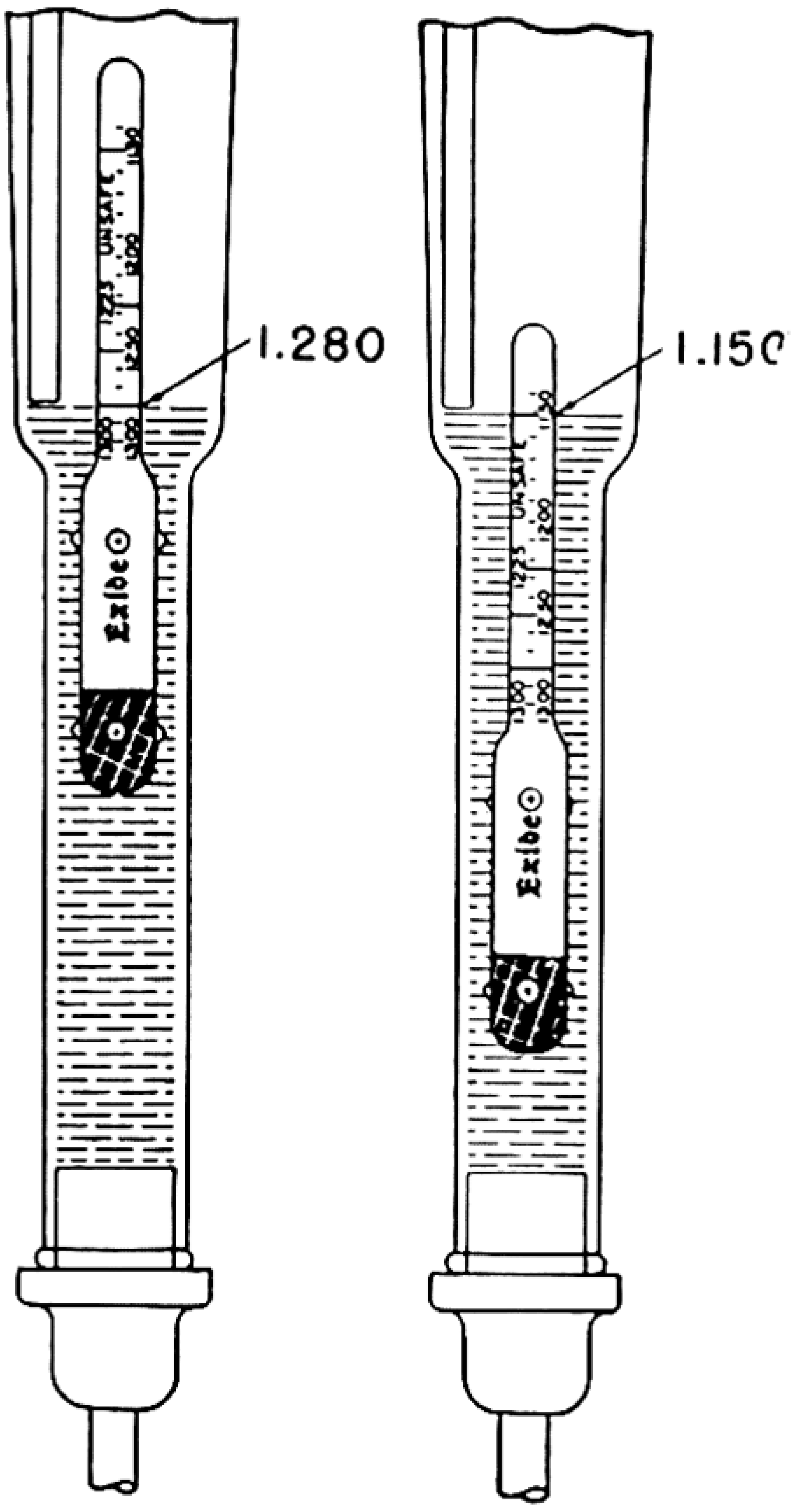


FIG. 2. Hydrometer. (*The Electric Storage Battery Company.*)

Example 1. A sample of hydrochloric acid has a specific gravity of 1.16. The percentage of HCl gas by weight is 31.45 per cent (from tables). Calculate the weight of HCl gas dissolved in 1,000 cc. of this acid.

Answer: $1{,}000 \text{ cc.} \times 1.16 \times \frac{31.45}{100} = 364.8 \text{ g. HCl}$

Example 2. Calculate the number of cubic centimeters of hydrochloric acid (specific gravity 1.16 containing 31.45 per cent HCl) required to furnish 20 g. pure HCl.

Answer: $20 \text{ g. HCl gas} \times \frac{100}{31.45} \times \frac{1}{1.16} = 54.7 \text{ cc. acid}$

Exercises

7. Calculate the weight of HCl gas dissolved in 500 ml. hydrochloric acid (specific gravity 1.131 containing 25.89 per cent HCl).

8. Calculate the volume in liters of hydrochloric acid (specific gravity 1.118 containing 29.13 per cent HCl) required to furnish 1,000 g. pure HCl.

9. Chlorides and Their Uses. A *chloride is a compound of chlorine with one other element (or radical).* Sodium, potassium, and magnesium chlorides are found in nature in large quantities. All metals and most nonmetals form chlorides. Ammonium chloride (sal ammoniac) is an example of a compound of chlorine with a positive radical. Potassium chloride is an important raw material for manufactured fertilizers. Magnesium chloride is used for the manufacture of special plasters and cements. Tin chloride is used in dyeing textiles. Mercuric chloride (corrosive sublimate) is a powerful poison often used as a germicide. Mercurous chloride (calomel) is used medically to stimulate organs producing secretions. Zinc chloride is used in treating paper and wood and also as a flux for soldering. Calcium chloride is used to dry gases, to settle dust on roads, and to prepare a brine that remains liquid at −48°C. Silicon tetrachloride may be used for forming smoke screens. Carbon tetrachloride is used in Pyrene fire extinguishers and in some nonflammable cleaning fluids. Sulfur monochloride, S_2Cl_2, is used in vulcanizing rubber.

10. Tests for Chloride Salts. All soluble chlorides when dissolved in water react with silver nitrate solution, $AgNO_3$, forming a white precipitate, AgCl, that will not dissolve in nitric acid. The reactions are shown by the equations:

$$\mathrm{NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3}$$
$$\mathrm{MgCl_2 + 2AgNO_3 \rightarrow 2AgCl\downarrow + Mg(NO_3)_2}$$

Exercise

9. Write equations for the reaction of silver nitrate with the chlorides of five different metals.

Chlorides also liberate HCl gas when they are treated with concentrated H_2SO_4, as indicated in Sec. 1.

SODIUM HYDROXIDE

11. Manufacture of Sodium Hydroxide by Electrolysis of Sodium Chloride Solution (Brine). The reaction that occurs during the passage of a direct electric current through sodium chloride solution is a complex one and may be represented by the following equation:

$$\mathrm{2NaCl + 2H_2O\ (+\ electric\ current) \rightarrow 2NaOH + H_2 + Cl_2}$$

It is to be noted (1) that water is involved in the reaction and (2) that, in addition to chlorine, two other products, sodium hydroxide and hydrogen, are also formed.

Chlorine collects at the anode while sodium hydroxide and hydrogen collect at the cathode. A number of cells designated by the name of the originators (Hooker, Vorce, Nelson, etc.) are used in the industrial electrolysis of brine. Although these cells differ in mechanical details of construction, the general principles of design and operation common to each are as follows: (1) the anode and cathode compartments are separate from each other to prevent interaction of the products, (2) the anode and cathode units are made of inert materials to prevent corrosion and consequent contamination of the products. A simplified sectional diagram of such a cell (Nelson type) is shown in Fig. 3. The solution of sodium chloride is fed into the anode compartment. Sodium hydroxide solution drips from the outer surface of the perforated steel cathode. Hydrogen is also collected from the outer compartment, and chlorine is drawn off from the anode compartment. A typical installation of cells (Hooker type) is shown in Fig. 4.

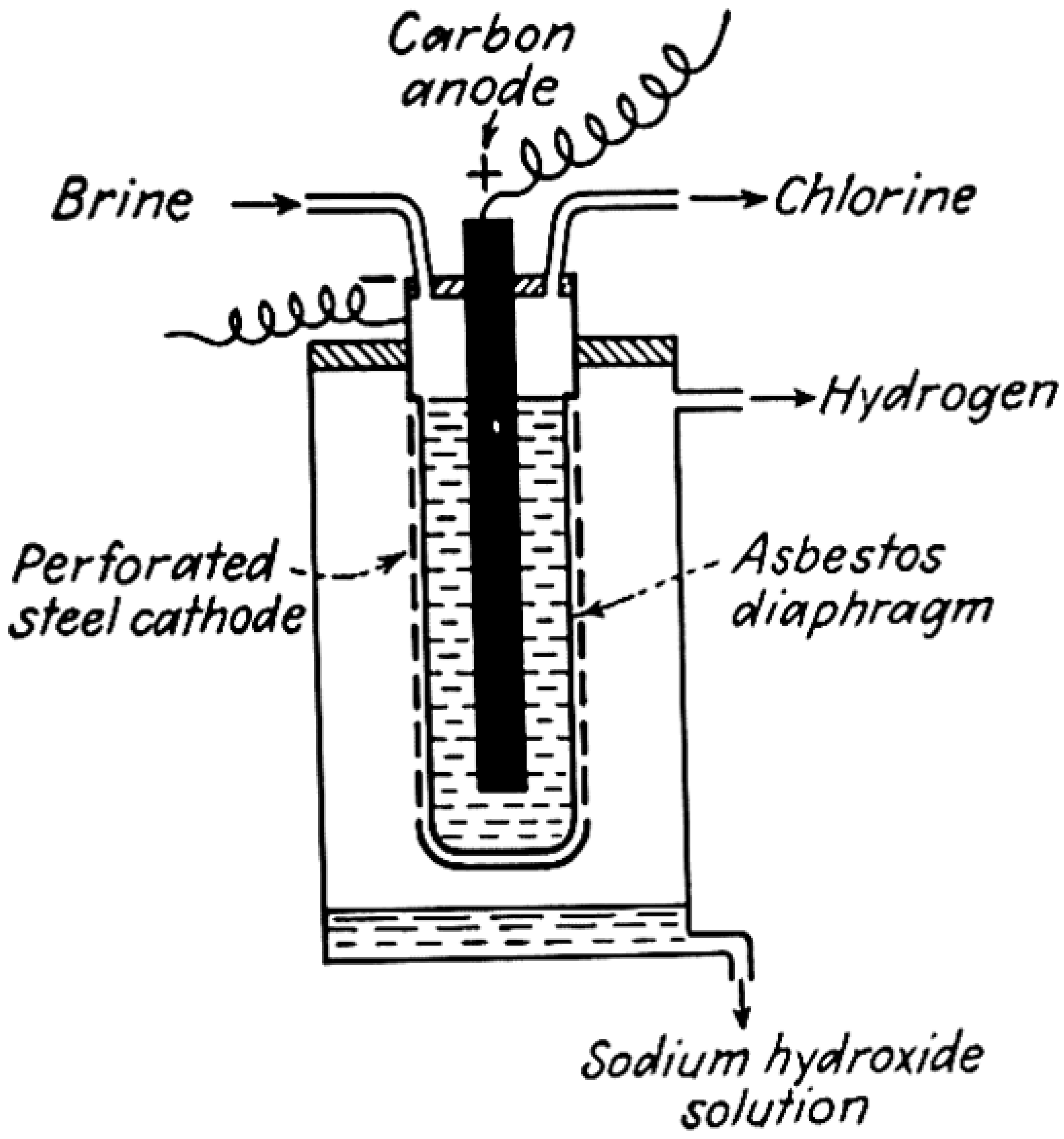


FIG. 3. Essential parts of cell for electrolysis of sodium chloride solution (Nelson type).

Exercise

10. Ten tons of sodium chloride is dissolved in water and decomposed by electrolysis. Calculate (*a*) the weight of water required for the reaction, (*b*) the weight of sodium hydroxide formed, (*c*) the weight of chlorine formed, (*d*) the amount of electric power used in kilowatt-hours (kw.-hr.), assuming that 3,100 kw.-hr. is required per ton of chlorine, (*e*) the cost of the electric power used at 1 cent per kilowatt-hour.

12. Hydroxides, Bases, and Alkalies.—A *hydroxide* or *base* is a compound which will neutralize acids and whose formula is recognized by the presence of a metal (or positive radical) and the OH radical. An *alkali* is a soluble, active base or hydroxide. The water solutions of alkalies are bitter to taste, slippery to touch, and turn red litmus blue.

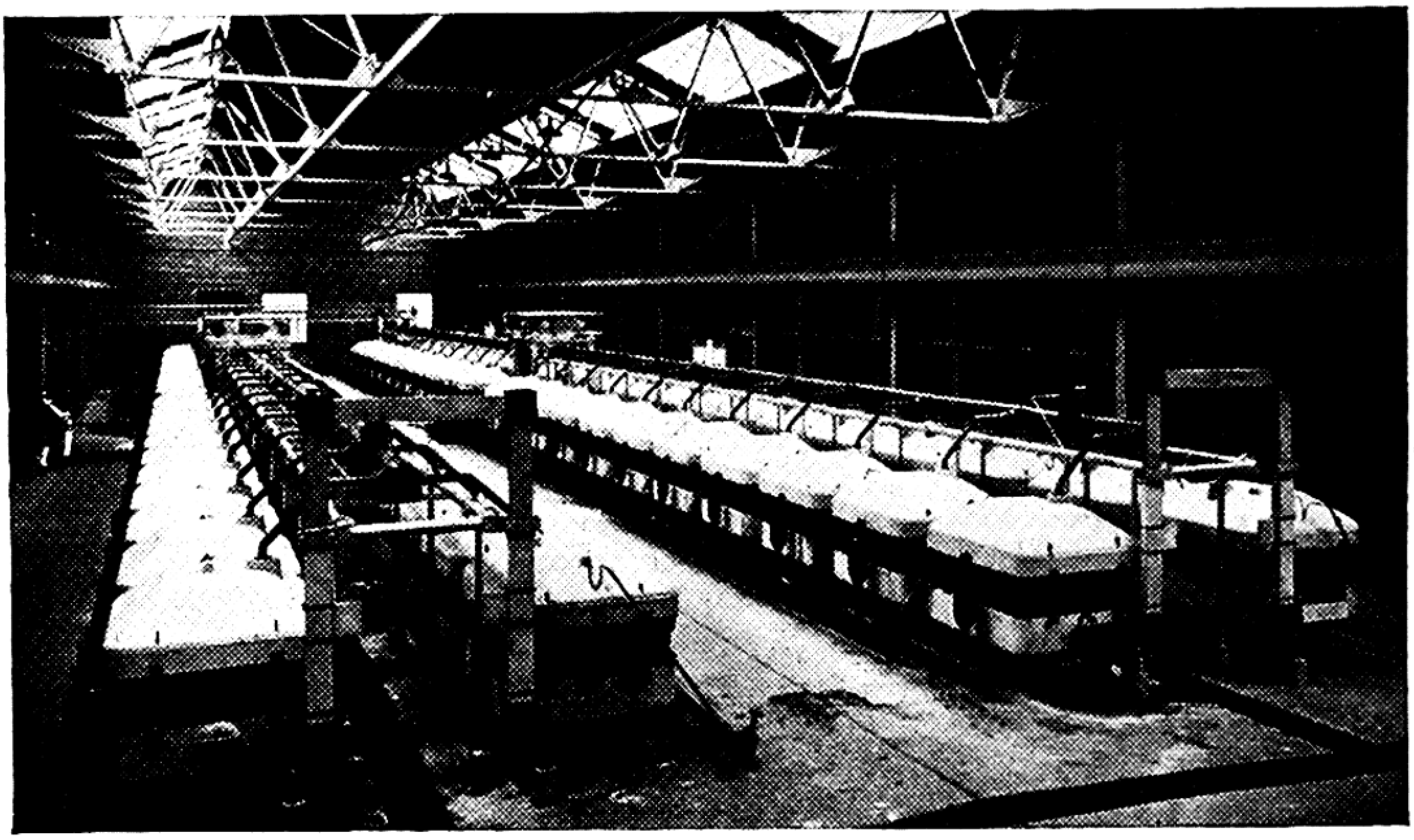


FIG. 4. Cells for electrolysis of sodium chloride solution (Hooker Type "S"). (*Hooker Electrochemical Company.*)

13. Physical Properties of Sodium Hydroxide (Caustic Soda or Lye). Sodium hydroxide is a white solid, very soluble in water. The solution has a slippery feeling and a soapy taste. It is generally used in the form of its water solution.

14. Chemical Properties of NaOH. Neutralization. These properties may be summarized by equations showing the reaction of NaOH with acids, forming salts and water (neutralization) and its reaction with salts forming insoluble hydroxides. It is one of the cheapest and most common bases and is widely used in industry.

Exercises

11. Write equations for the reaction of NaOH with each of the following acids: (*a*) HCl, (*b*) H_2SO_4, (*c*) HNO_3, (*d*) H_2SO_3, (*e*) H_2CO_3, (*f*) H_3PO_4, (*g*) $HC_2H_3O_2$, (*h*) HBr, (*i*) H_2SO_4, (*j*) H_2S.

12. Write an equation for the reaction of NaOH with $CuCl_2$ to form $Cu(OH)_2$ and NaCl.

13. Using the equation of Exercise 12 as a model, write equations for the reaction of NaOH with the salts (in solution) of five different metals. Keep in mind that these reactions are reversible and will not proceed toward completion

unless one of the products is precipitated. Use Table IV in the Appendix to determine whether or not a compound will precipitate.

SUGGESTED READING

———, Electrolytic Chlorine and Caustic Soda, *Chem. & Met. Eng.*, **49**, 114 (December, 1942).

STUART, LYSTER, and MURRAY, The Story of the Hooker Cell, *Chem. & Met. Eng.*, **45**, 354 (1938).

CHAPTER IX

STRUCTURE OF ATOMS AND IONS. IONIZATION

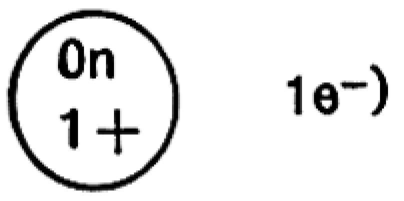
In the preceding chapters, we have learned to write the formulas of many different substances. At this point, it is desirable for us to consider why elements combine according to definite patterns or "formulas," and the nature of the combining forces. Related to these questions, the concept of valence has already been considered but only in a limited sense. As a further step, we are to study some of the principles of atomic and molecular structure. Although much of our information in this field has been acquired through the investigations of physicists, this knowledge is of great importance to the chemist in the study of the formation and the properties of compounds.

1. Examples of Regularity in Chemical Formulas. The number and kind of atoms that combine to form compounds may vary widely as illustrated by the following formulas: H_2O, CaO, Fe_2O_3, CO_2, P_2O_5, SO_3, Mn_2O_7, OsO_4; HCl, $CaCl_2$, $FeCl_3$, CCl_4, PCl_5, SCl_6.

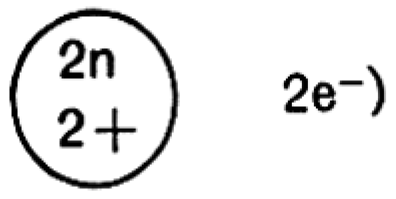
There are, however, certain regularities in formulas as is evidenced by H_2O, Ag_2O, Cu_2O, Hg_2O, Au_2O, Tl_2O, Na_2O, K_2O; HCl, $AgCl$, $CuCl$, $HgCl$, $AuCl$, $TlCl$, $NaCl$, KCl; CaO, MgO, BaO, SrO, ZnO, FeO, MnO, NiO, CoO, PbO, SnO, HgO; $CaCl_2$, $MgCl_2$, $BaCl_2$, $SrCl_2$, $ZnCl_2$, $FeCl_2$, $MnCl_2$, $NiCl_2$, $CoCl_2$, $PbCl_2$, $SnCl_2$, $HgCl_2$.

2. Atomic Structure. The explanation for these similarities and differences lies in the structure of the atoms of the various elements. The combined efforts of chemists, physicists, and mathematicians during the past 40 years have shown that an atom is composed of a positively charged central *nucleus* surrounded by a number of (negative) *electrons*, e^-, or *unit negatively charged particles.* The simplest atom is that of hydrogen, which consists of a nucleus with a single positive charge, and around this nucleus is a single electron. The helium atom has a nucleus with a double positive charge, and around this nucleus are 2 electrons. The oxygen atom has a nucleus with a charge of eight, and 8 electrons outside of this nucleus. Two of these electrons are in a first *level* or *orbit* quite close to the nucleus, while the other six are in a second level farther removed from the nucleus. Practically all of the mass or weight of an atom is concentrated at the nucleus, so that the nucleus has a mass nearly identical with the atomic weight of the element. It is convenient to represent the structures of atoms as follows:

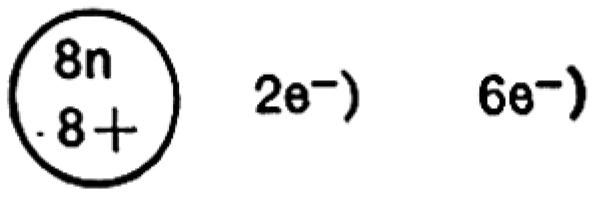
Hydrogen atom



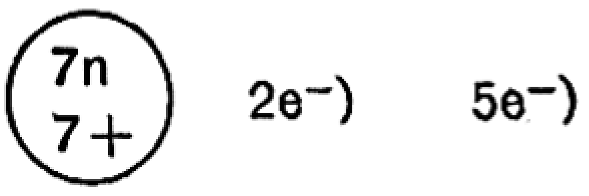
Helium atom



Oxygen atom



Nitrogen atom



Such diagrams may be easily constructed for any element with atomic number less than 21 by observing the following relationships:

a. The mass of the nucleus is nearly equal to the atomic weight of the element. The nucleus contains two kinds of units: the neutrons, *n* (unit neutral particles), and protons, *p* or + (unit positively charged particles). The sum of the neutrons and protons approximately equals the mass or atomic weight.

b. The charge on the nucleus is always positive and equals the atomic number of the element. (Atomic numbers may be found by reference to the same tables that give atomic weights. See inside front cover of this book.) *The atomic number is the net positive charge in the nucleus of the atom.*

c. The total number of electrons outside the nucleus (external electrons) equals the atomic number.

d. The first level never contains more than 2 electrons.

e. The second level never contains any electrons until the first level has its full quota of 2 electrons.

f. The second level never contains more than 8 electrons.

g. The third level never contains any electrons until the second level has its full quota of 8 electrons.

h. The third level never contains more than 8 electrons in any of the elements with atomic number less than 21.

i. The fourth level never contains any electrons unless the third level has at least 8 electrons.

Structures and diagrams can be worked out for elements of atomic number higher than 20, but the relationships become somewhat more complicated and in many cases more than one structure is possible.

The arrangement of the external electrons is ascertained, mainly from studies by physicists, of the light rays (spectra) emitted by various elements. The nature of the light emitted depends upon the location of the electrons, and thus it is possible to determine the location of the electrons by a careful analysis of the light, using a spectroscope to determine the wave length of the light.

Exercises

1. Construct diagrams for the structures of atoms of each of the elements with atomic numbers less than 21. Consult the table inside the front cover of this book for the necessary atomic weights and atomic numbers.

3. Valence Electrons and Electron Symbols. The electrons in the outermost level are called *valence electrons* for reasons explained in the following section. Most of the chemical properties of elements depend upon the valence electrons, and it is convenient to use simplified atomic structure diagrams (electron symbols) showing only the valence electrons and the symbol of the element, such as

$$\mathrm{H}\cdot \qquad :\mathrm{C}: \qquad :\dot{\mathrm{N}}: \qquad :\ddot{\mathrm{O}}:$$

By reference to the valence table in the Appendix, such electron symbols can be constructed for any element, even if details of atomic structure are unknown. Thus, the electron symbol for zinc is Zn: and Ag· is the electron symbol for silver.

Exercises

2. Construct electron symbols for the elements K, Na, H, Ca, B, Mg, P, Si.

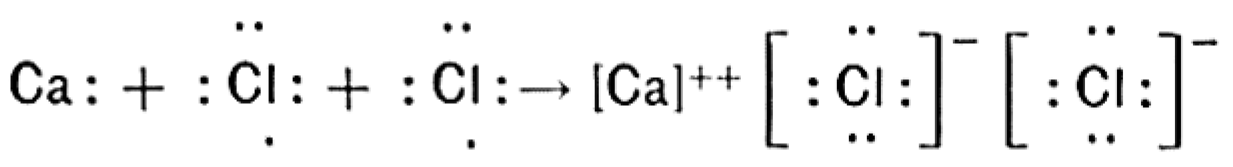
3. Construct electron symbols for Pb, Ca, Sn, Fe, Cu, and Hg, assuming in each case that the number of valence electrons is the same as the maximum positive valence of the element.

4. Formation of Ions. *An ion is an electrically charged atom or radical.* Atoms having 1, 2, or 3 valence electrons have a tendency to lose all these to any other atom that will accept them. Atoms having 4 or more valence electrons have a tendency to gain or share enough additional electrons from other atoms so that they have a total of 8 electrons in the outermost level. Compound formation, and the number of atoms that combine to make a molecule, may be explained in terms of a very marked tendency for atoms to gain, lose, or share their valence electrons from, to, and with one another. Thus, if sodium and chlorine atoms are brought together, the sodium loses an electron and the chlorine gains an electron.

$$\underset{\text{sodium atom}}{\mathrm{Na}\cdot} \;+\; \underset{\text{chlorine atom}}{\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:} \;\rightarrow\; \underset{\text{sodium ion}}{[\mathrm{Na}]^{+}} \; \underset{\text{chloride ion}}{\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\right]^{-}}$$

As a result, the sodium atom bears a positive charge. Such a particle is called a *sodium ion* while the chlorine atom bears a negative charge (*chloride ion*). The 2 ions are then attracted to one another, and a compound NaCl results because of the unlike electrical charges.

If calcium atoms and chlorine atoms are brought together, a similar change occurs but 2 chlorine atoms must be involved so that the calcium atom may lose both of its valence electrons.



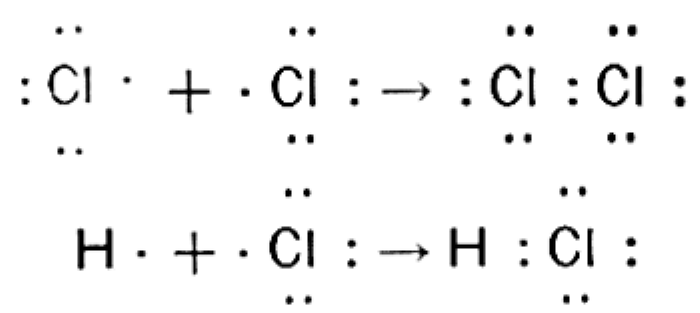
$$\mathrm{Ca}: + :\overset{..}{\underset{.}{\mathrm{Cl}}}: + :\overset{..}{\underset{.}{\mathrm{Cl}}}: \rightarrow [\mathrm{Ca}]^{++}\left[:\overset{..}{\underset{..}{\mathrm{Cl}}}:\right]^{-}\left[:\overset{..}{\underset{..}{\mathrm{Cl}}}:\right]^{-}$$

Thus, the compounds NaCl and $CaCl_2$ are accounted for, and, in a similar way, many other formulas may be written. The failure of sodium and calcium to combine is also explained by the fact that both these elements have a tendency to lose electrons and neither has a tendency to gain electrons.

Exercise

4. Use electron symbols to obtain correct formulas (if you think a compound can be formed) for the following: (*a*) lead (2 valence electrons) and oxygen, (*b*) lead (4 valence electrons) and oxygen, (*c*) magnesium and oxygen, (*d*) lead and mercury, (*e*) potassium and chlorine.

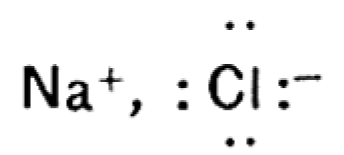
There are many instances in which atoms unite because of a sharing of their electrons rather than an actual gain and loss. Typical examples are as follows:



$$:\overset{..}{\underset{..}{\mathrm{Cl}}}\cdot + \cdot\overset{..}{\underset{..}{\mathrm{Cl}}}: \rightarrow :\overset{..}{\underset{..}{\mathrm{Cl}}}:\overset{..}{\underset{..}{\mathrm{Cl}}}:$$

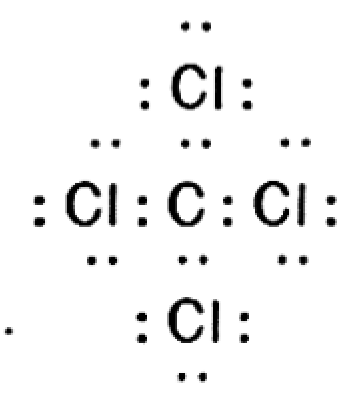
$$\mathrm{H}\cdot + \cdot\overset{..}{\underset{..}{\mathrm{Cl}}}: \rightarrow \mathrm{H}:\overset{..}{\underset{..}{\mathrm{Cl}}}:$$

Elements with 1 or 2 valence electrons form their compounds by actual loss of electrons to some other atom or group of atoms. Elements with 4 or more electrons usually form compounds either by gain (the usual case when the number of valence electrons of the other element is 1 or 2) or by sharing when the number of valence electrons of the other element is 4 or more. Compounds formed as the result of gain and loss of electrons are called *electrovalent* or *ionic compounds* and are distinctly different in character from the *covalent compounds* formed as a result of sharing of electrons. Typical electrovalent and covalent compounds are illustrated as follows:



$$\mathrm{Na^+,\ :\overset{..}{\underset{..}{Cl}}:^-}$$

NaCl
electrovalent type



$$\begin{array}{c} \mathrm{:\overset{..}{Cl}:} \\ \mathrm{:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{C}}:\overset{..}{\underset{..}{Cl}}:} \\ \mathrm{:\underset{..}{Cl}:} \end{array}$$

CCl_4
covalent type

It is to be noted that the electrovalent (NaCl) type of compound contains ions and that the covalent (CCl_4) type does not contain ions. Bases and salts are, in general, electrovalent in character. Sugar, alcohol, carbon tetrachloride, and related substances are of the covalent type. Experiments show that water solutions of electrovalent compounds conduct the electric current. Such solutions are known as *electrolytes.* Covalent compounds in general do not conduct the electric current and are therefore called *nonelectrolytes* (see Secs. 6 and 10).

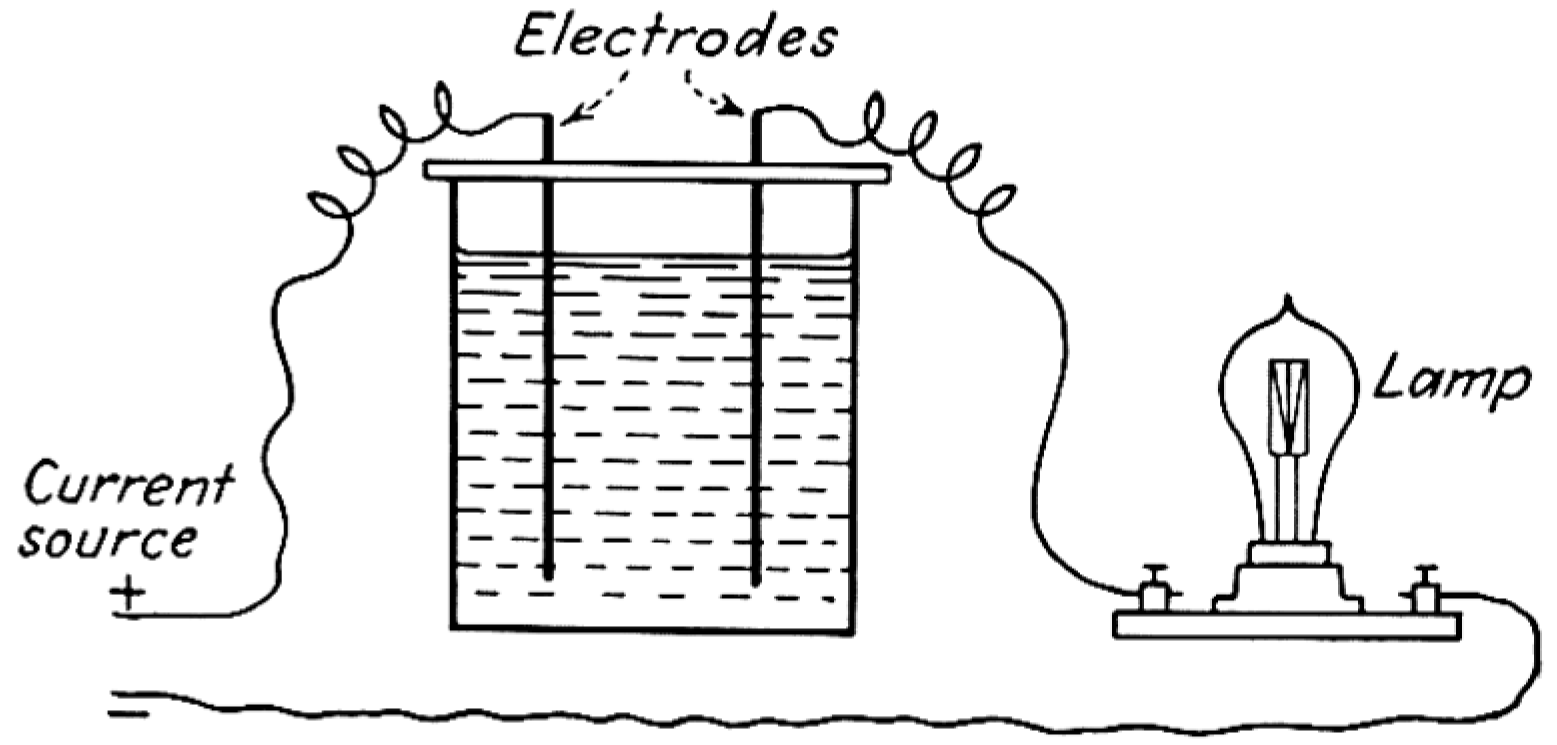


FIG. 1. Apparatus for testing conductivity.

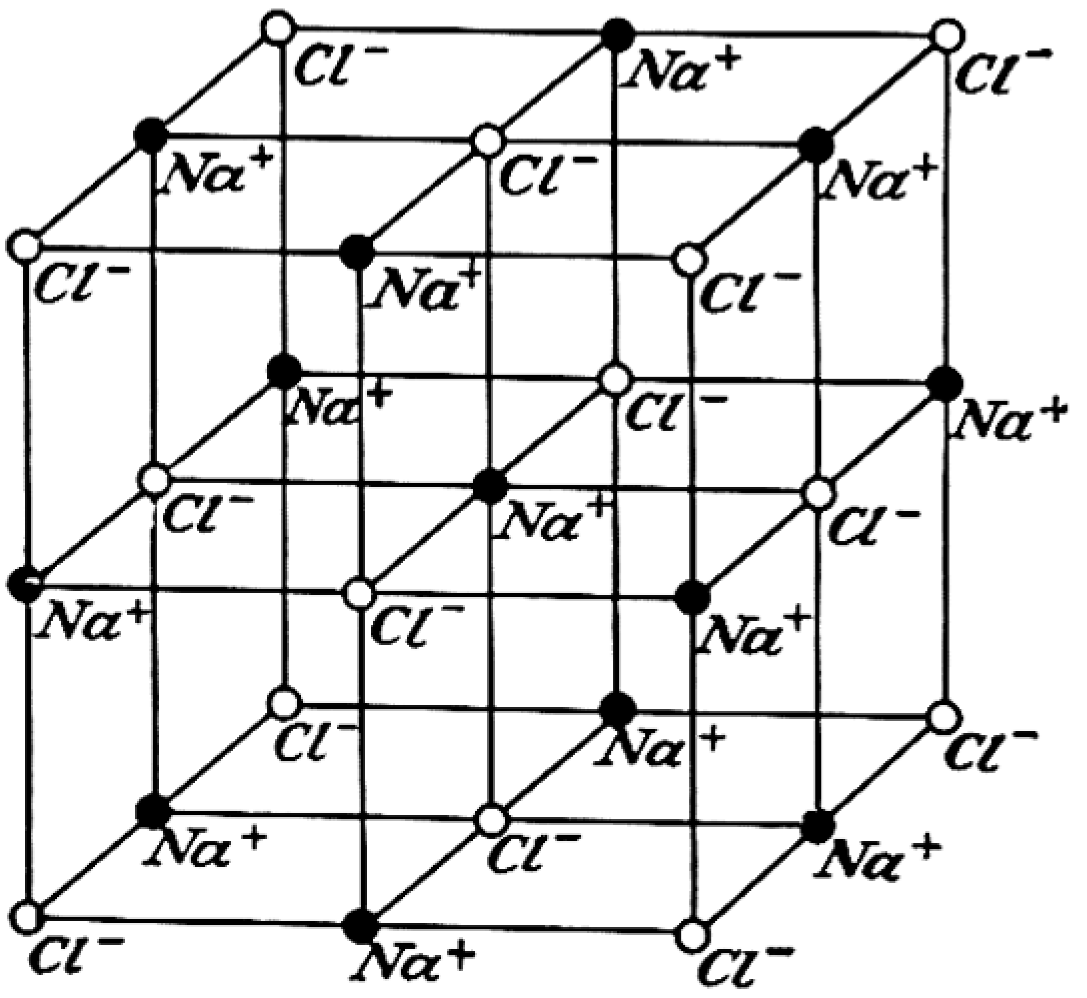


FIG. 2. Crystal structure of NaCl.

5. Structure of Sodium Chloride. By means of X-ray photography it is possible to study the structure of the crystals of sodium chloride and other compounds. The photographs, thus obtained and known as *diffraction patterns,* when mathematically interpreted, show definite structural arrangements of ions in space rather than separate molecules. The structure of the sodium chloride crystal is represented by the diagram shown in Fig. 2. This type of structure is known as the *cubic* *space lattice.* Each sodium ion is surrounded at equal distances by 6 chloride ions. (Note the central ion.) The ions appear to be held rigidly in position in the space lattice by electrostatic forces between them. This type of arrangement extends completely through the crystal in an unbroken pattern of three dimensions.

A simplified diagram of one side of the cubic lattice of sodium chloride indicating the relative positions of Na^+ and Cl^- ions is shown in Fig. 3. It is to be noted that the lines in the diagram (Fig. 2) have no physical counterpart in the actual crystal. The lines may, however, be regarded as analogous to the electrostatic forces that hold the ions in position in the crystal.

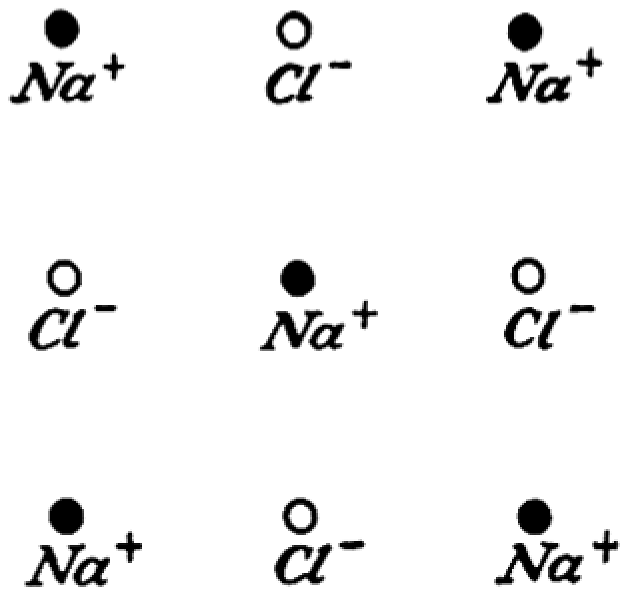


FIG. 3. Crystal structure of NaCl (plane projection of the central plane).

It is evident from the preceding discussion that sodium chloride (and other electrovalent compounds) in the crystal state are composed of definite arrangements of *ions.* We may, therefore, write the unit formulas $[\overset{+}{\text{Na}}\overset{-}{\text{Cl}}]$, $[K^+Cl^-]$, etc.

IONIZATION

6. Properties of Water Solutions of Salts, Acids, and Bases. It was previously stated that water solutions of electrovalent compounds conduct the electric current and that solutions of covalent compounds (sugar, alcohol, etc.) generally do not conduct the electric current. It is also known that solutions of electrovalent compounds freeze at lower temperatures and boil at higher temperatures than solutions of covalent compounds of the same molar concentration (Table I).

These two properties, with other properties to be considered later, are the basis for the principle of *electrolytic dissociation* or *ionization of electrolytes,* first proposed by Arrhenius (1887). This principle may be stated as follows: *Acids, bases, salts in water solution, dissociate (separate) into electrically charged particles (ions).* The term *ion,*[1] a Greek word meaning "wanderer," was used in the sense that the ions are free to move about in the solution. This is apparently due to the fact that water acts as an insulator between the ions and apparently attracts them away from the solid crystal. A general equation to indicate the dissociation is the following:

---

[1] It is to be noted that Arrhenius had no knowledge of the structure of ions. This field of chemistry and physics was not developed until about 30 years later. "Bound" ions exist in the electrovalent compounds before the latter are dissolved.

$$A^+B^- \rightarrow A^+ + B^-$$

That acids, bases, and salts in water solution conduct the electric current is explained by the fact that the ions bear electric charges through the solution. When the current is passing through a solution of copper chloride, *e.g.*, copper ions, Cu^{++}, move toward the negative terminal (cathode) and are therefore called *cations;* chloride ions, Cl^-, move toward the positive terminal (anode) and are called *anions.*

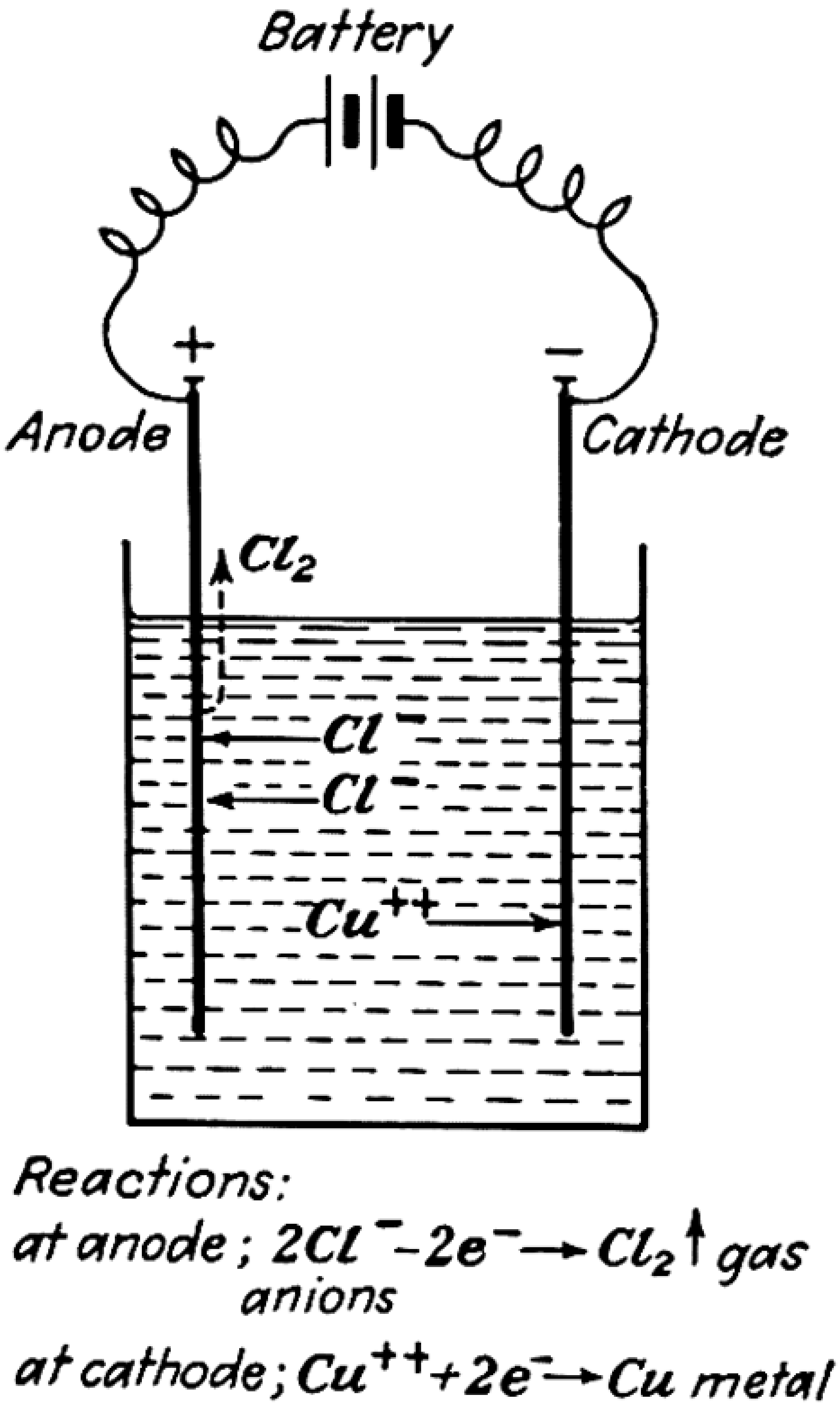

Battery
+
−
Anode
Cathode
Cl₂
Cl⁻
Cl⁻
Cu⁺⁺
Reactions:
at anode; 2Cl⁻ − 2e⁻ → Cl₂↑ gas
anions
at cathode; Cu⁺⁺ + 2e⁻ → Cu metal

Fig. 4. Electrolysis of copper chloride.

The conductivity of an electrolyte depends chiefly upon three factors:

a. The number of ions in the solution.

b. The rate of movement (mobility) of the ions.

c. The electric charge on the ions (H^+, Cu^{++}, etc.).

As a simple analogy to the foregoing principles, one may think of a group of people to be transported in boats across a lake. The number of people transported in a given time will depend upon

a. The number of boats available.

b. The speed at which the boats move.

c. The capacity of the boats.

That the freezing and the boiling points of acids, bases, and salts in water solution are lower and higher, respectively, than those of sugar, alcohol, etc., at the same molar concentration (Table I) is explained by the presence of the greater number of particles (ions) in solutions of acids, bases, and salts. (These effects are explained in detail in more advanced textbooks.)

7. Distinction between Atoms and Ions. When an atom of sodium changes to a sodium ion, there is a loss of 1 electron:

$$\underset{\text{atom}}{Na} - 1e^- \rightarrow \underset{\text{ion}}{Na^+}$$

TABLE I*

Substance	*Freezing Points of* 0.1*M Solutions*, °C.
Nonelectrolytes:	
Alcohol	−0.184
Glycerin	−0.186
Sugar	−0.188
Electrolytes:	
NaCl	−0.348
HCl	−0.356
KNO_3	−0.330
$BaCl_2$	−0.478
Na_2SO_4	−0.459

* HILDEBRAND, "Principles of Chemistry," 5th ed., p. 129.

Because of the difference in structure, sodium atoms (or sodium metal) have properties quite different from the properties of sodium ions, as indicated by the following comparisons:

Sodium Metal (Na)	*Sodium Ion* (Na^+)
Exists in the free state	Exists in a crystal or in a solution of a compound containing also a negative ion
Soft metal	Colorless
Very active with water	Inactive with water
Electrically neutral	Positively charged

The properties of chlorine gas, Cl_2, likewise, differ very much from the properties of chloride ions, Cl^-.

Chlorine Gas (Cl_2)	*Chloride Ion* (Cl^-)
Exists in the free state as a gas	Exists in a crystal or in a solution of a compound containing also a positive ion
Diatomic molecules, Cl_2	Single units, Cl^-
Greenish-yellow color	Colorless
Disagreeable odor	Odorless

Exercises

5. In terms of electrons, explain the difference between a positive ion, *e.g.*, Na^+, and a negative ion, *e.g.*, Cl^-.

6. Write symbols for (*a*) the hydrogen atom, the hydrogen ion, (*b*) the magnesium atom, the magnesium ion, (*c*) the aluminum atom, the aluminum ion, (*d*) the tin atom, the stannic tin ion, (*e*) the sulfur atom, the sulfide ion. (Consult the valence table in the Appendix; also IX. 9.)

NOTE: The charge on an ion is due to the gain or loss of electrons by the corresponding atom.

8. Colors of Ions. Many of the common ions are colorless. This property is easily observed in salts or in solutions containing these ions.

A number of the metallic ions, however, have characteristic colors, *e.g.*, the blue copper ion, Cu^{++}. Solutions of copper chloride, $CuCl_2$, copper sulfate, $CuSO_4$, and copper nitrate, $Cu(NO_3)_2$, are all blue in color. It is known that ions in solution are often combined with water (hydrated ions), *e.g.*, $(Cu \cdot 4H_2O)^{++}$. Solutions of ferrous iron salts containing Fe^{++} and solutions of nickel salts containing Ni^{++} are green in color.

9. Symbols for Ions. In the study of valence (Chap. III) it was noted that the valence number is indicated by positive and negative signs, *e.g.*, Na^+, Ca^{++}, Cu^{++}, OH^-, SO_4^{--}. From our knowledge of atomic structure, we can understand the origin of these numbers. For convenience in writing equations for ionic reactions, it is necessary to review the valence numbers or ionic charges for the common ions listed below.

Positive Ions
Hydrogen ion, H^+
Sodium ion, Na^+
Potassium ion, K^+
Ammonium ion, NH_4^+
Silver ion, Ag^+
Calcium ion, Ca^{++}
Magnesium ion, Mg^{++}
Aluminum ion, Al^{+++}
Ferric ion, Fe^{+++}
Stannic ion, Sn^{++++}

Negative Ions
Hydroxyl ion, OH^-
Chloride ion, Cl^-
Nitrate ion, NO_3^-
Bicarbonate ion, HCO_3^-
Carbonate ion, CO_3^{--}
Bisulfate ion, HSO_4^-
Sulfate ion, SO_4^{--}
Phosphate ion, PO_4^{---}

10. Electrolytes and Nonelectrolytes. From the standpoint of the theory of ionization, substances may be divided roughly into three classes, as follows:

Strong Electrolytes. Substances which, in water solution, are good conductors of electricity and are highly or completely ionized. Typical examples of this class are sodium chloride, potassium nitrate, nitric acid, sodium hydroxide. With some exceptions, the strong electrolytes are of the electrovalent or ionic type.

Weak Electrolytes. Substances which, in water solution, are poor conductors of electricity and are slightly ionized. Examples of this class are acetic acid and ammonium hydroxide. (Water is so very slightly ionized that it also may be regarded as a nonelectrolyte.)

Nonelectrolytes. Substances which, in water solution, do not conduct the electric current and are not ionized. Examples are alcohol, sugar, glycerin; also carbon tetrachloride, benzene, and toluene which are not soluble in water. These compounds are of the covalent or nonionic type.

Typical strong and weak electrolytes are listed in Table II. This information is necessary in the writing of ionization equations and should be carefully studied.

TABLE II

Strong Electrolytes (*in Water Solutions*) (Many free ions)	*Weak Electrolytes* (*in Water Solutions*) (Few free ions)
Strong or active acids: HCl, HNO_3, H_2SO_4	Weak acids: $HC_2H_3O_2$, H_2CO_3, H_3BO_3 HCN, H_2S, etc.
Strong or active bases: NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$	Weak base: NH_4OH
Many soluble salts: NaCl, $NaNO_3$, Na_2SO_4, KBr, Na_2CO_3, $Cu(NO_3)_2$, etc.	Some soluble salts (form few ions): $Pb(C_2H_3O_2)_2$, $HgCl_2$, etc. Water, H_2O (very weak)
All "insoluble" salts dissolve to some extent. The dissolved portions are highly ionized.	

11. Solubility of Common Substances. Solubility Rules. The following statements regarding the solubility of common substances will be found useful in the study of ionization and other topics in chemistry and should be memorized.

a. Nearly all salts of sodium, potassium, and ammonium are soluble.

b. All nitrates and acetates are soluble.

c. All chlorides are soluble except AgCl, HgCl, $PbCl_2$. ($PbCl_2$ is relatively soluble in hot water.)

d. All sulfates are soluble except $BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$.

e. All sulfides are insoluble except Na_2S, K_2S, $(NH_4)_2S$.

f. All carbonates and phosphates are insoluble except those of sodium, potassium, and ammonium and certain acid phosphates, $Ca(H_2PO_4)_2$, etc.

g. All hydroxides are insoluble except NaOH, KOH, NH_4OH. $Ca(OH)_2$, and $Ba(OH)_2$ are of intermediate solubility.

Exercises

7. Make a list of 10 soluble compounds and 10 insoluble compounds (use formulas and names).

8. Make a list of 10 strong electrolytes and 10 weak electrolytes (use formulas and names).

12. Ionization Equations. Acetic acid, $HC_2H_3O_2$, the acid found in vinegar, is a typical weak electrolyte which is only slightly ionized. From conductivity and freezing-point data, it can be calculated that a 0.1 N solution of acetic acid is 1.3 per cent ionized. This information can be indicated by the following equation:

$$\underset{98.7\%}{HC_2H_3O_2} \rightleftharpoons \underset{1.3\%}{H^+ + C_2H_3O_2^-}$$

In organic chemistry, the formula for acetic acid is written, CH_3COOH. Using this formula, the equation is

$$\underset{98.7\%}{CH_3COOH} \rightleftharpoons \underset{1.3\%}{CH_3COO^- + H^+}$$

The arrows in these equations indicate the extent of the dissociation into separate ions. The short arrow pointing to the right indicates that there are relatively few hydrogen ions and acetate ions; the long arrow pointing to the left indicates that a large proportion of the acetic acid molecules are not dissociated, in accordance with the percentages shown below the equation.

Another weak acid is carbonic acid, H_2CO_3, and the ionization is represented in two steps, as follows:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad \text{(primary carbonate ion)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \qquad \text{(secondary carbonate ion, or normal carbonate ion)}$$

For the ionization of a weak base, ammonium hydroxide, NH_4OH, an equation can be written as follows:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

It is to be observed here, also, that the short arrow pointing to the right indicates that but few ions are present in the solution; the long arrow pointing to the left shows that a large proportion of the ammonium hydroxide is undissociated.

In water solutions of strong electrolytes, *e.g.*, sodium chloride, $NaCl$, and sodium iodide, NaI, the solid crystals, upon dissolving, are considered to be completely dissociated into separate ions, at least in dilute solutions. It was shown in Fig. 2 that ions exist also in the solid crystal lattice. The ionization equation showing the dissociation of an electrovalent compound can be represented thus (see Sec. 6):

$$A^+B^- \rightarrow A^+ + B^-$$

or

$$\overset{+}{Na}\overset{-}{Cl} \rightarrow Na^+ + Cl^-$$

The *effective concentration* of the "free" ions in the more concentrated solutions of salts, NaCl, etc, however, is not 100 per cent of the quantity of salt dissolved. This conclusion is based upon conductivity and freezing-point data. Because of complicating factors commonly referred to as *interionic attractions, clustering effects, drag effects*, etc. we can indicate the general ionization equation thus,

$$A^+B^- \rightleftarrows A^+ + B^-$$

The short arrow pointing to the left indicates that not all the ions are entirely free from each other; *i.e.*, the effective concentration of the free ions is not 100 per cent. The expressions, A^+B^- and $\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{Cl}}$, represent the ions of the crystal lattice. In writing ionization equations these charges are often omitted. In such cases, however, the ionic character of the substances should be kept in mind. The ionization equations for several strong electrolytes follow:

$$\begin{aligned}
&Na_2{}^+SO_4{}^{--} && \rightleftarrows 2Na^+ && + SO_4{}^{--}\\
&Cu^{++}(NO_3)_2{}^- && \rightleftarrows Cu^{++} && + 2NO_3{}^-\\
&K_2{}^+CrO_4{}^{--} && \rightleftarrows 2K^+ && + CrO_4{}^{--}\\
&Ca^{++}(OH)_2{}^- && \rightleftarrows Ca^{++} && + 2OH^-\\
&H_2{}^+SO_4{}^{--} && \rightleftarrows 2H^+ && + SO_4{}^{--}\\
&HCl^* && \rightleftarrows H^+ && + Cl^-
\end{aligned}$$

Exercises

9. Write ionization equations for potassium nitrate, KNO_3; zinc sulfate, $ZnSO_4$; hydrogen sulfide, H_2S; potassium hydroxide, KOH; aluminum sulfate, $Al_2(SO_4)_3$.

10. Classify the compounds in Exercise 9 as (*a*) acids, bases, salts, (*b*) strong or weak electrolytes.

The facts and principles presented in this chapter should be thoroughly reviewed as they have a direct application in Chap. X.

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* For further consideration of this equation refer to X. 5 and 13.

CHAPTER X

IONIC REACTIONS. ACIDS, BASES, AND SALTS

In Chap. IX it was pointed out that the ions of bases and salts, in water solution, dissociate or break away from their positions in the original lattice structure. We shall now study some of the reactions in solutions containing ions, and we shall also learn more about the nature and the properties of acids and bases. The study of acids and bases is an important field in chemical research, with a wide application in the chemistry of soils, the corrosion of metals, and other applied fields of investigation.

1. Ionic Reactions. Since all acids, bases, and salts (V. 9) in water solution exist at least partially in the form of ions, practically all the reactions in such solutions involve the ions of the acids, bases, and salts. Thus the equation usually written

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 \qquad \text{(molecular equation)}$$

is actually incomplete since it ignores entirely the existence of the ions of NaCl, $AgNO_3$, and $NaNO_3$. For this reason, the equations for reactions between dissolved acids, bases, and salts are frequently written in the form of ionic equations as explained in the following sections.

2. Ionic Equations for Double Decomposition (Precipitation). The ionic equation for the reaction of NaCl with $AgNO_3$ may be written as follows:

$$\text{Full ionic equations}\left\{\begin{tikzcd}
NaCl \arrow[r, shift left] & Na^+ \arrow[l, shift left] & + & Cl^- \\
AgNO_3 \arrow[r, shift left] & NO_3^- \arrow[l, shift left] \arrow[d, shift left] & + & Ag^+ \arrow[d, shift right] \\
 & NaNO_3 \arrow[u, shift left] & & AgCl\downarrow \arrow[u, shift right]
\end{tikzcd}\right.$$

The long arrow pointing toward the AgCl indicates that there will be but few Ag^+ and Cl^- ions in the solution after mixing.

The arrow pointing downward to the right of AgCl indicates that the AgCl is a precipitate.

Such a scheme shows all the ions that may be present and also indicates their relative concentrations. At the instant of mixing, the concentrations of all 4 ions are relatively high, but Ag^+ and Cl^- concentrations are rapidly reduced as the precipitate of AgCl is formed. The concentration of Na^+ and NO_3^- ions remains unchanged.

The ionic equation given above may be simplified by indicating the ions present in large number and obtaining

$$\begin{array}{lcl} Na^+ & + & Cl^- \\ NO_3^- & + & Ag^+ \\ & & \big\downarrow\uparrow \\ & & AgCl\downarrow \end{array}$$

Since Na^+ and NO_3^- take no important part in the reaction, this equation may be further simplified to

$$Ag^+ + Cl^- \rightleftarrows AgCl\downarrow$$

which is known as a simple ionic equation.

Exercises

1. Write (*a*) molecular, (*b*) full ionic, (*c*) simple ionic equations for each of the following reactions in solution: zinc chloride with silver nitrate; aluminum chloride and silver nitrate; barium chloride and sulfuric acid; barium nitrate and potassium sulfate; sodium hydroxide and copper sulfate. Be sure that each ion has the proper charge and formula, that the entire equation balances throughout, and that all long and short arrows are in the proper direction. (Refer to solubility rules IX. 11.)

2. List the ions that remain nearly unchanged in concentration in each of the above reactions. Then list the ions whose concentrations are lowered to a marked extent in each reaction.

3. Complete and Incomplete Double Decomposition. Double decomposition reactions will be *complete* when a precipitate, a gas, or a slightly ionized substance such as water is formed. However, if NaCl and KNO_3, for example, are mixed, little, if any, reaction takes place. An ionic equation indicates the reason for this behavior.

$$\begin{array}{l} NaCl \rightleftarrows Na^+ \quad + Cl^- \\ KNO_3 \rightleftarrows NO_3^- + K^+ \end{array} \qquad \text{or} \qquad \underbrace{\begin{array}{l} Na^+ \quad + Cl^- \\ NO_3^- + K^+ \end{array}}_{\text{no reaction}}$$

Since both possible products are soluble and highly or completely ionized, there is no combination of ions that will unite to form a new substance, and reaction fails to occur.

A double decomposition will also be more or less *incomplete* if one or more of the starting materials are insoluble (gas or precipitate) or slightly ionized. The extent of the incompleteness varies with the insolubility or ionization of the aforesaid starting materials. For example, there is practically no reaction between HNO_3 and AgCl because of the low solubility of AgCl.

4. Properties of Salts from the Point of View of Ionization. From the point of view of ionization, all soluble chloride salts can be studied as a group; all such solutions behave similarly in many ways because chloride ions are present in all cases. Likewise, the study of other salts reduces itself to the study of their ions. A knowledge of the characteristic properties of a relatively few ions makes it possible to predict the behavior of a large number of salts.

5. Properties of Acids and Bases from the Point of View of Ionization. All acids possess many properties in common, such as sour taste and the turning of blue litmus to red. From the point of view of ionization these properties are easily explained. All acid solutions contain hydrogen ion,[1] H^+, and therefore all acid solutions act similarly on litmus and have many other properties in common. These are the properties of hydrogen ion. A solution that contains a high concentration of hydrogen ion has these properties to a marked extent, while a solution containing a low concentration has these properties to a lesser extent. Solutions of bases contain the hydroxyl ion, OH^-, and therefore possess properties in common, such as soapy taste, changing red litmus to blue, and neutralization of acids. The chemistry of acids, bases, and salts in water solution thus reduces itself to the study of the ions of these substances.

6. Neutralization. For some purposes, it is satisfactory to define neutralization as the reaction between an acid and a base, producing a salt and water. From the point of view of the ionic theory, neutralization is the union of hydrogen ion with hydroxyl ion to form water.

$$H^+ + OH^- \rightleftarrows H_2O$$

Modern theoretical chemistry defines acids, bases, and neutralization in a broader manner (Sec. 13).

7. Ionic Equations for Neutralization. The ionic equation for the neutralization of HCl by NaOH may be written:

$$\begin{tikzcd}
NaOH \rightleftarrows & Na^+ & + OH^- \\
HCl \rightleftarrows & Cl^- \arrow[d, shift right] & + H^+ \arrow[d, shift left] \\
& NaCl \arrow[u, shift right] & H_2O \arrow[u, shift left]
\end{tikzcd}$$

or

$$\begin{tikzcd}
Na^+ & + OH^- \\
Cl^- & + H^+ \arrow[d, shift left] \\
& H_2O \arrow[u, shift left]
\end{tikzcd}$$

or

$$H^+ + OH^- \rightleftarrows H_2O$$

---

[1] It is known that the hydrogen ion, H^+, is hydrated, $H^+ \cdot H_2O$, or H_3O^+ (hydronium ion) in water solution. For simplicity, however, the ion will be designated by the symbol, H^+, in this book (Sec. 13).

Another example is

$$\begin{tikzcd}[column sep=small]
2NaOH \arrow[r, phantom, "\rightleftharpoons"] & 2Na^+ & + & 2OH^- & & & 2Na^+ & + & 2OH^- \\
H_2CO_3 \arrow[r, phantom, "\leftrightharpoons"] & CO_3^{--} \arrow[d, shift left] & + & 2H^+ \arrow[d, shift right] & \text{or} & H_2CO_3 \arrow[r, phantom, "\leftrightharpoons"] & CO_3^{--} & + & 2H^+ \arrow[d, shift right] \\
& Na_2CO_3 \arrow[u, shift left] & & 2H_2O \arrow[u, shift right] & & & & & 2H_2O \arrow[u, shift right]
\end{tikzcd}$$

The slight ionization of one of the starting materials (H_2CO_3 in the last example) prevents the complete simplification of an ionic equation.

Exercise

3. Write (*a*) molecular, (*b*) full ionic, (*c*) simplified ionic equations for the reactions: $KOH + H_2SO_4$; $NH_4OH + HNO_3$; $Zn(OH)_2 + HCl$; $Fe(OH)_3 + H_2SO_4$; $NaOH + H_3PO_4$.

8. Titration. Titration is the process of measuring the concentration of a solution by allowing it to react with some other standard solution. A standard solution is a solution of known concentration, *e.g.*, 1*N* HCl. Titration of solutions of acids and bases is known as *acidimetry* or *alkalimetry*.

If, for example, it is desired to measure the normality (VII. 19) of a solution of NaOH, this solution is poured into a long graduated glass tube with a stopcock at one end. Such a tube is known as a *buret*. The buret containing 50 or 75 ml. of the NaOH solution up to the zero mark is secured in a vertical position by a suitable clamp on a stand. A known volume (10 or 20 ml.) of standard HCl solution (1*N* or 0.1*N*) is then measured into a beaker which is placed underneath the stopcock of the buret. A few drops of litmus or phenolphthalein indicator solution is added to the solution in the beaker. A glass stirring rod is used to ensure thorough mixing of the indicator and the acid. The stopcock of the buret is opened cautiously, and the sodium hydroxide solution is slowly added to the acid. When the neutralization or "end point" is reached, the indicator will change color (red to blue with litmus; colorless to pink with phenolphthalein). For practical reasons, the HCl solution is sometimes placed in the buret, and the NaOH solution is measured from a graduate or pipette into the beaker.

Calculation of the normality of the NaOH solution is based upon the fact that 1 l. of a normal solution of an acid contains 1.008 g. of ionizable hydrogen, and 1 l. of a normal solution of a base contains 17.008 g. of ionizable hydroxyl radical. These quantities are chemically equivalent as indicated by the equation:

$$\begin{array}{ccccc} H^+ & + & OH^- & \rightleftarrows & H_2O \\ 1.008 \text{ g.} & & 17.008 \text{ g.} & & 18.016 \text{ g.} \end{array}$$

or

$$\begin{array}{ccc} 1 \text{ g.} & 17 \text{ g.} & 18 \text{ g.} \end{array}$$

Since water is an extremely weak electrolyte, the above reaction is almost quantitatively complete in neutralization. That it is not absolutely complete is shown by hydrolysis (Sec. 9), the reverse of neutralization.

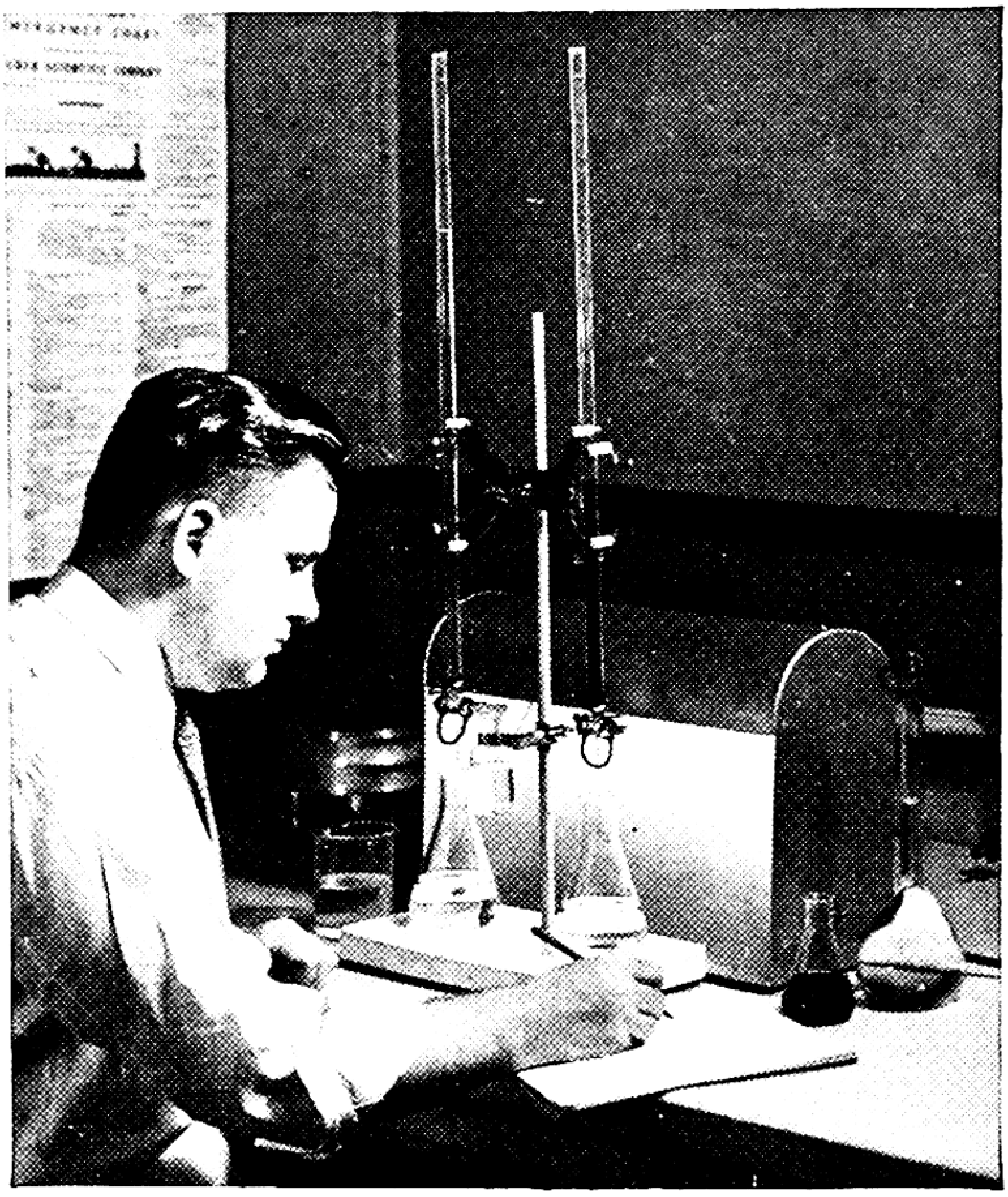


FIG. 1. Apparatus used in titration. (*Fisher Scientific Company.*)

From the above equation, it is clear that 1 l. of a 1N solution of an acid will neutralize 1 l. of a 1N solution of a base, that 10 ml. of a 1N solution of HCl will neutralize 100 ml. of a 0.1N solution of a base, etc. From such relationships, it follows that the volumes of acid and base used are inversely proportional to their normalities, or

ml. of acid : ml. of base : : normality of base : normality of acid

Substituting the values given above, we have,

10 ml. acid : 100 ml. base : : 0.1N of base : 1N of acid

In a proportion, the products of the means and extremes are equal, or

$$(100 \text{ ml. base})(0.1N \text{ of base}) = (10 \text{ ml. acid})(1N \text{ of acid})$$

or

$$10 = 10$$

or

$$(\text{ml. of base})(\text{normality of base}) = (\text{ml. of acid})(\text{normality of acid})$$

Exercises

4. How many milliliters of 1N HCl are required to neutralize 25 ml. of 0.4N NaOH?

5. 40 ml. of 1N HCl are required to neutralize 10 ml. of KOH. What is the normality of the KOH solution? What is the weight of KOH dissolved in the 10 ml. of KOH solution?

9. Hydrolysis of a Salt. This may be defined as the reaction of water with ions of a salt producing an acid and a base. Thus, it is the reverse of neutralization. It is almost always an incomplete reaction. A molecular equation for the hydrolysis of sodium carbonate is

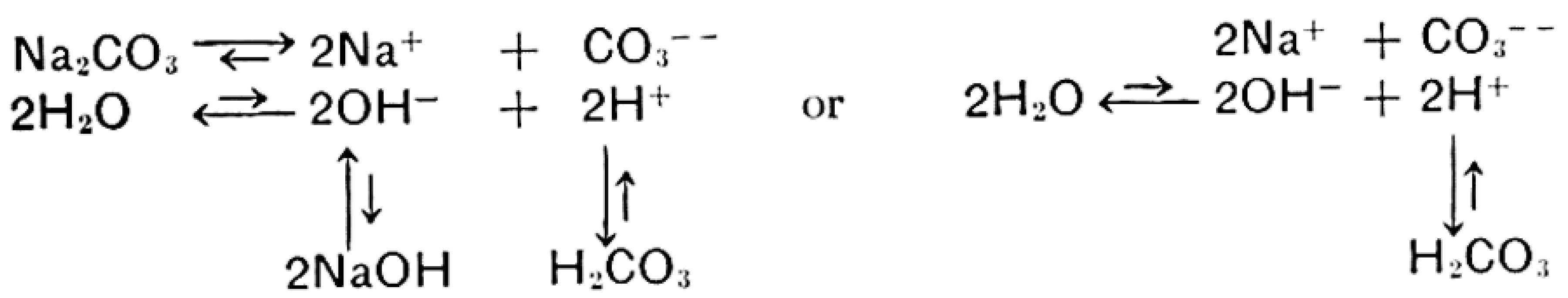
$$Na_2CO_3 + 2H_2O \rightleftarrows 2NaOH + H_2CO_3$$

Hydrolysis of salts causes some salt solutions to act either acidic or basic toward litmus and other indicators.

Exercise

6. Write molecular equations for the hydrolysis of (*a*) $CuSO_4$, (*b*) $FeCl_3$, (*c*) $KC_2H_3O_2$, (*d*) Na_2S, (*e*) $ZnCl_2$.

10. Ionic Equations for Hydrolysis. The ionic equation for the hydrolysis of Na_2CO_3 may be written:



$$\begin{array}{llll} Na_2CO_3 & \rightleftarrows 2Na^+ & + & CO_3^{--} \\ 2H_2O & \rightleftarrows 2OH^- & + & 2H^+ \\ & \quad\updownarrow & & \updownarrow \\ & 2NaOH & & H_2CO_3 \end{array} \qquad \text{or} \qquad \begin{array}{llll} & 2Na^+ & + & CO_3^{--} \\ 2H_2O \rightleftarrows & 2OH^- & + & 2H^+ \\ & & & \updownarrow \\ & & & H_2CO_3 \end{array}$$

It is to be observed that H^+ unites with CO_3^{--} to form H_2CO_3 because the latter is a weak acid. The result is that an excess of OH^- (over H^+) is present in the Na_2CO_3 solution.

Indicators are sensitive to excess of OH^- or H^+, but are not affected by molecules of acids or bases.

Exercises

7. What color would you expect litmus to show in a Na_2CO_3 solution?

8. Write (*a*) full and (*b*) simplified ionic equations for the hydrolysis of each of the salts of Exercise 6. State whether each of these salt solutions would contain excess H^+ or OH^- and predict the behavior of the solutions toward litmus.

9. List two salts (other than those indicated above) whose water solutions will be (*a*) acidic (*b*) basic, (*c*) nearly neutral toward litmus.

10. Why would it be harmful practice to use sea water containing $MgCl_2$ in steam boilers? (Write ionic equations.)

11. Sheet iron is often treated with $ZnCl_2$ solution to remove the oxide film before it is galvanized. This process is known as *pickling*. Show, by ionic equations, why the $ZnCl_2$ solution would serve as a pickling solution. Consider the reaction

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{+++} + 3H_2O$$

11. Ionic Equations for Displacement. The ionic equation for the reaction of Zn with $CuSO_4$ solution may be written thus:

$$Zn + Cu^{++} + SO_4^{--} \rightarrow Cu + Zn^{++} + SO_4^{--}$$

or, more simply, since the SO_4^{--} ion takes no part in the action,

$$Zn + Cu^{++} \rightarrow Cu + Zn^{++}$$

The mechanism of this change is made clear by a consideration of the atomic structure of the ions and atoms involved.

12. Displacement in Terms of Atomic Structure. During displacement each zinc atom loses 2 electrons and becomes a zinc ion and each copper ion gains 2 electrons and becomes a copper atom. In terms of simplified atomic structure diagrams, the equation is

$$[Zn:]^0 + [Cu]^{++} \rightarrow [Cu:]^0 + [Zn]^{++}$$

or

$$\begin{aligned} Zn \quad - 2e^- &\rightarrow Zn^{++} \\ Cu^{++} + 2e^- &\rightarrow Cu \end{aligned}$$

The order in which metals "displace" or discharge ions of other metals follows the activity series (V. 8), known also as the electromotive series.

Exercises

12. Explain why a solution of copper sulphate should not be made in a galvanized-iron tank.

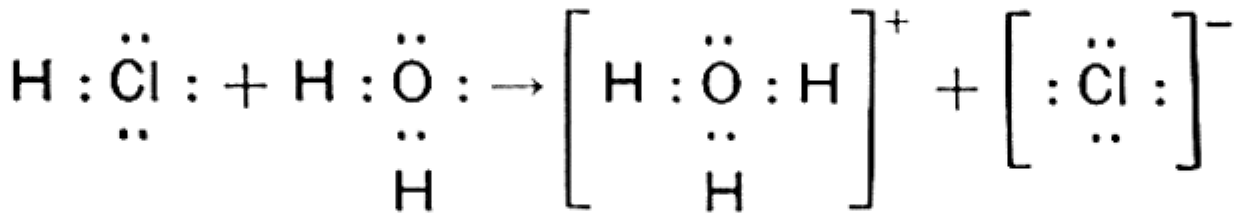
13. Write (*a*) molecular and (*b*) simple ionic equations for those of the following combinations in which ionic displacement will take place: $Al + AgNO_3$; $Mg + CuSO_4$; $Ag + NaNO_3$; $Pb + AgNO_3$; $Mg + CrCl_3$.

NOTE: Sections 13 and 14 may be assigned at the discretion of the instructor.

13. Other Concepts of Acids and Bases. The work of Fajans, Goldschmidt, and others has shown that the hydrogen ion, H^+, of acids does not exist free in solution as such, but rather in the hydrated or solvated form known as the hydronium ion, $H^+ \cdot H_2O$, or H_3O^+. The fact that the H^+ or proton (+ unit of electricity) is extremely small and reactive with water explains the existence of the hydronium ion. To simplify the writing of equations, it is convenient to use the term H^+ as it was done in previous sections. The formation of hydronium ion from HCl is illustrated by the following equation:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \qquad (1)$$

or, using electronic formulas,



$$H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: + H:\underset{H}{\overset{\cdot\cdot}{O}}: \rightarrow \left[H:\underset{H}{\overset{\cdot\cdot}{O}}:H\right]^+ + \left[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\right]^-$$

in analogy with the formation of ammonium ions;

$$\underset{\text{ammonia}}{NH_3} + H_2O \rightarrow NH_4^+ + OH^- \qquad (2)$$

Lowry and Brönsted define acids as *proton donors* and bases as *proton acceptors.* In Eq. (1), for example, HCl (proton donor) is an acid and H_2O (proton acceptor) is a base. In Eq. (2), however, H_2O (proton donor) is an acid and NH_3 (proton acceptor) is a base. This concept of acids and bases is useful in connection with work in nonaqueous solutions.

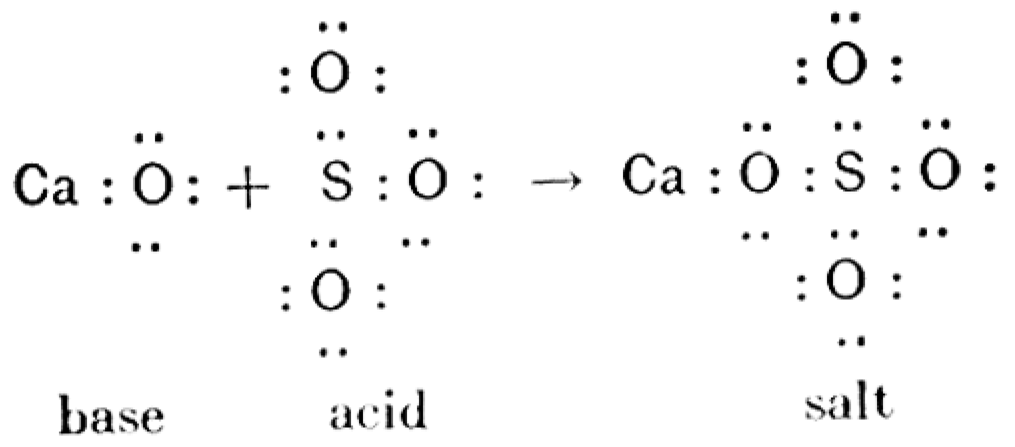
Another system of acids and bases of an earlier origin, and useful in mineralogy, is based upon the relative basic and acidic properties of a series of oxides. For example,

basic neutral acidic
Na_2O, CaO, Al_2O_3, H_2O, SiO_2, CO_2, SO_3

The basic oxide, CaO, for example, combines readily with the acidic oxide, SO_3, forming $CaSO_4$.

$$CaO + SO_3 \rightarrow CaSO_4$$

or, in terms of electronic formulas,



$$Ca:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: + \underset{:\underset{\cdot\cdot}{O}:}{\overset{\overset{\cdot\cdot}{:O:}}{S}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: \rightarrow Ca:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{:\underset{\cdot\cdot}{O}:}{\overset{\overset{\cdot\cdot}{:O:}}{S}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

From the above equation, it is seen that the base, CaO, contributes 2 electrons to the acid, SO_3, which, of course, gains or accepts the 2 electrons. In this system of bases and acids (the G. N. Lewis system), the base is an *electron donor* and the acid is an *electron acceptor.* This classification of bases and acids may be extended to other types of reactions, for example,

$$KCl + AlCl_3 \rightarrow KAlCl_4$$

Exercise

14. Rewrite the equation for the reaction of KCl with $AlCl_3$ using electronic formulas as in the reaction of CaO with SO_3.

It is obvious from the foregoing discussion that the field of acids and bases is a large one. The choice of a classification of acids and bases depends upon what application is to be made of it. The original H^+, OH^- concept of acids and bases, devised by Arrhenius for water solutions, appears to be simple and practical in the study of water solutions and is, therefore, used in this textbook.

14. Hydrogen Ion Concentration, pH, Indicators. There are many reactions and processes that depend upon the acidity or hydrogen-ion concentration. In the reactions that take place in the tanning of skins, the decomposition of sewage, the treatment of boiler waters, the corrosion of metals, and the digestion of food in the body, the concentration of hydrogen ion is an important factor.

The Danish chemist Sörensen proposed the pH system for expressing the low hydrogen-ion concentrations in biochemical reactions. This system may be represented by the following scale of pH values:

pH 1 2 3 4 5 6 7 8 9 10 11 12 13 14
↑
←——————neutral——————→
increasing acidity (pure water) increasing alkalinity

The basis of the pH scale is discussed below. The measurement of pH may be done by indicators as shown in Table I, or by means of various instruments known as pH meters (Fig. 2).

Water solutions of all acids contain an excess of H^+ (hydrogen ions) and water solutions of all bases contain an excess of OH^- (hydroxyl ions). The concentration of the ions in a given solution will, of course, depend upon the dilution and the extent of the ionization of the acid or base.

Water is a neutral substance. It does, however, contain both H^+ and OH^- ions. The ionization equation is as follows:

$$H_2O \rightleftarrows H^+ + OH^-$$

In pure water the concentration of each of these ions has been found to be $1 \times 10^{-7}N$ (or $0.0000001N$). According to the mass law,[1]

$$[H^+] \times [OH^-] = K$$

the product of the molar concentrations of these ions in water is

$$[1 \times 10^{-7}] \times [1 \times 10^{-7}] = 1.0 \times 10^{-14}$$

Upon this basis, it is clear that, if the C_{H^+} is greater than 10^{-7}, the solution is acid; if less than 10^{-7}, the solution is alkaline. For example, a solution containing $1 \times 10^{-4}N$ H^+ ion and $10^{-10}N$ OH^- will be acid; a solution containing $1 \times 10^{-10}N$ H^+ and $1 \times 10^{-4}N$ OH^- will be alkaline.

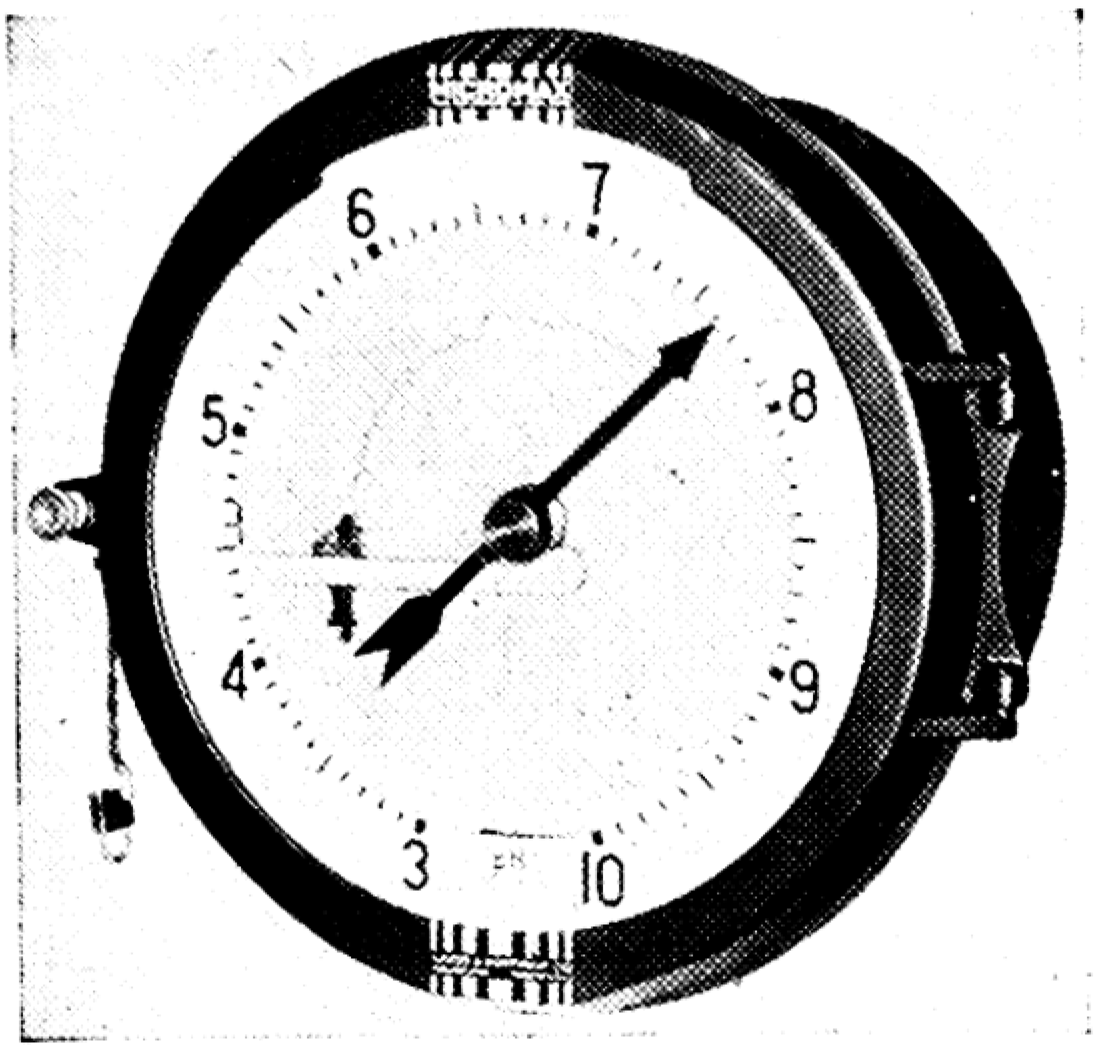


Fig. 2. pH or hydrogen-ion recorder. *(Leeds and Northrup Company.)*

Table I shows the color changes of various indicators at definite concentrations of H^+ and OH^- ions and the corresponding pH values.

Note that a pH of 1 indicates that the solution contains 10^{-1} or 1×10^{-1} or $0.1N$ H^+, that a pH of 7 indicates that the solution is neutral (pure water). The pH of human blood is 7.35. Is blood acid or alkaline? What is the pH of a solution containing $1 \times 10^{-14}N$ H^+? What is the OH^- ion concentration in such a solution? The pH value is defined mathematically as the logarithm of the reciprocal of the hydrogen-ion concentration or,

$$\text{pH} = \log \frac{1}{C_{H^+}}$$

---

[1] Or, law of molecular concentration. Refer to Chemical Equilibrium in larger textbooks of general chemistry.

TABLE I
APPROXIMATE INDICATOR COLORS*

b = blue, *c* = colorless, *g* = green, *o* = orange, *r* = red, *y* = yellow, *v* = violet, *t* = transition

Conc. of H^+	Conc. of OH^-	pH†	Methyl violet	Methyl orange	Brom-phenol blue	Brom-cresol green	Lit-mus	Brom-thymol blue	Thy-mol blue	Phenol-phthal-ein	Aliza-rin yellow R	Indi-go car-mine	Solutions of certain common substances
1	10^{-14}	0	*y*	*r*	*y*	*y*	*r*	*y*	*r*	*c*	*y*	*b*	1*M* HCl
10^{-1}	10^{-13}	1	*g*	*r*	*y*	*y*	*r*	*y*	*o*	*c*	*y*	*b*	0.1*M* HCl
10^{-2}	10^{-12}	2	*b*	*r*	*y*	*y*	*r*	*y*	*y*	*c*	*y*	*b*	
10^{-3}	10^{-11}	3	*v*	*r*	*y*	*y*	*r*	*y*	*y*	*c*	*y*	*b*	0.05*M* $HC_2H_3O_2$
10^{-4}	10^{-10}	4	*v*	*o*	*g*	*y*	*r*	*y*	*y*	*c*	*y*	*b*	H_2CO_3 (CO_2 at 1 atm.)
10^{-5}	10^{-9}	5	*v*	*y*	*b*	*g*	*r*	*y*	*y*	*c*	*y*	*b*	0.2*M* NH_4Cl
10^{-6}	10^{-8}	6	*v*	*y*	*b*	*b*	*r*	*y*	*y*	*c*	*y*	*b*	
10^{-7}	10^{-7}	7	*v*	*y*	*b*	*b*	*t*	*g*	*y*	*c*	*y*	*b*	"Neutral point"
10^{-8}	10^{-6}	8	*v*	*y*	*b*	*b*	*b*	*b*	*y*	*c*	*y*	*b*	1*M* $NaHCO_3$
10^{-9}	10^{-5}	9	*v*	*y*	*b*	*b*	*b*	*b*	*g*	*t*	*y*	*b*	0.2*M* $NaC_2H_3O_2$
10^{-10}	10^{-4}	10	*v*	*y*	*b*	*b*	*b*	*b*	*b*	*r*	*y*	*b*	
10^{-11}	10^{-3}	11	*v*	*y*	*b*	*b*	*b*	*b*	*b*	*r*	*o*	*b*	0.05*M* NH_4OH
10^{-12}	10^{-2}	12	*v*	*y*	*b*	*b*	*b*	*b*	*b*	*r*	*r*	*b*	0.4*M* Na_2CO_3
10^{-13}	10^{-1}	13	*v*	*y*	*b*	*b*	*b*	*b*	*b*	*r*	*r*	*g*	0.1*M* NaOH
10^{-14}	1	14	*v*	*y*	*b*	*b*	*b*	*b*	*b*	*r*	*r*	*y*	1*M* NaOH

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* HILDEBRAND: "Principles of Chemistry," 4th ed., p. 171. By permission of The Macmillan Company.

† pH is an abbreviated designation of the concentration of H^+ much used in biological work. Its meaning is obvious from the table.

or as the negative logarithm of the H^+ ion concentration,

$$pH = -\log C_{H^+}$$

For the reader who is not familiar with logarithms, pH may be defined as the exponent of the hydrogen-ion concentration with the negative sign omitted.[1]

SUGGESTED READING

BARNES, Evidence for the Complete Dissociation of Salts at All Concentrations in Aqueous Solutions, *J. Chem. Education*, **13**, 428 (1936).

BRISCOE, Teaching the New Concepts of Acids and Bases in General Chemistry, *J. Chem. Education*, **17**, 128 (1940).

JOHNSON, The Advantages of the Older Methods, *J. Chem. Education*, **17**, 132 (1940).

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[1] The foregoing discussion of hydrogen-ion concentration is reproduced from "Experiments in General Chemistry," 8th ed. (1917) p. 44, by Chandlee, Mack, and Currier, with the permission of the authors.

CHAPTER XI

CHLORINE, OXIDATION AND REDUCTION

Chlorine may be regarded as the most important member of the halogen (salt-forming) family of elements, fluorine, chlorine, bromine, iodine. It is an extremely reactive element and is never found free in nature. Salts of chlorine, *e.g.*, KCl and NaCl, are found abundantly as natural deposits. Sodium chloride is the chief industrial source material in the production of chlorine by the electrolysis of brine (VIII. 11).

1. Physical Properties. The greenish-yellow color and disagreeable choking odor of chlorine gas are very characteristic physical properties and serve to identify the element. It is poisonous when breathed in any quantity and should be kept confined in closed containers. Laboratory work with chlorine should be done under hoods. Chlorine is heavier than air and can be liquefied at 6.6 atm. and 18°C. To conserve space, chlorine is generally shipped in the liquid form in cylinders or in tank cars.

Exercise

1. Calculate the relative density of chlorine, Cl_2, and air. (The weight of 1 l. of chlorine is 3.17 g. The weight of 1 l. of air is 1.29 g., both at S.T.P.)

2. Chemical Properties. Chlorine resembles oxygen in a general way because it unites so readily with such a large number of other elements.

Chlorine also reacts with many compounds, including water, sodium hydroxide, potassium iodide, and hydrocarbons such as turpentine, $C_{10}H_{16}$. Chlorine reacts with cold water forming hypochlorous acid, HClO or HOCl.

$$H_2O + Cl_2 \rightleftarrows HCl + HOCl$$

This reaction is reversible and incomplete. If the solution is exposed to sunlight, HOCl is decomposed and oxygen is liberated. Chlorine reacts with steam as follows:

$$\overset{\text{steam}}{2H_2O} + 2Cl_2 \rightleftarrows 4HCl + O_2$$

This reaction is also incomplete; in fact, in the past the reverse reaction was used as an industrial method for preparing chlorine (Deacon process).

If chlorine is passed into cold sodium hydroxide solution, both the HCl and the HOCl are neutralized and NaCl and sodium hypochlorite, NaOCl, are formed.

If chlorine is passed into potassium iodide solution, iodine is liberated and potassium chloride is formed.

This reaction may be used as a test for chlorine since even a minute quantity of iodine gives a brown color. The test may be made even more sensitive by having starch present. An intense blue color is observed in the presence of starch. This so-called *iodine-starch test* is familiar to the student of biology. Iodine in compounds and iodide ion both fail to give the blue color with starch. Chlorine will slowly bleach the blue color.

When chlorine is passed over lime, $Ca(OH)_2$, bleaching powder, CaClOCl, is formed.

Exercises

2. Write equations for the reactions of chlorine with five other elements, including two nonmetals.

3. Balance the following equation:

$$NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$

4. Balance the following equation indicating the ions:

$$Cl_2 + KI \rightarrow I_2 + KCl$$

5. In which of the following combinations would a blue color be obtained: (*a*) KCl, KI and starch solution, (*b*) Cl_2, I_2 and starch solution, (*c*) NaCl, I_2 and starch solution, (*d*) Cl_2, KI and starch solution, (*e*) HCl, KI and starch solution, (*f*) I_2 and starch solution, (*g*) Cl_2 and starch solution, (*h*) NaCl and starch solution, (*i*) KI and starch solution?

6. Write the equation for the formation of bleaching powder.

3. Industrial Uses. Chlorine is used for sterilizing and disinfecting water and for bleaching cotton and linen textiles, paper, and wood pulp; also for the manufacture of compounds that serve as disinfectants or bleaching agents. Smaller amounts are used in the recovery of tin from tin plate, and in the preparation of chemicals such as Prestone and neoprene rubber, as well as many common chlorides, CCl_4, etc. The total production capacity of chlorine manufacturing plants in the United States in 1940 was more than 650,000 tons.

Exercise

7. Name and give formulas of five chlorides (VIII. 9).

4. Bleaching with Chlorine. That dry chlorine does not act as a bleaching agent is easily demonstrated. In the presence of moisture, the following reaction occurs:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

The hypochlorous acid thus formed is the real bleaching agent. It bleaches the dye by oxidation as shown in the following equation:

$$\underset{\substack{\text{indigo} \\ \text{(a blue dye)}}}{C_{16}H_{10}N_2O_2} + 2HOCl \rightarrow 2HCl + \underset{\substack{\text{isatin} \\ \text{(a colorless substance)}}}{2C_8H_5NO_2}$$

In general, this reaction may be summarized thus,

$$\text{(Dye molecule)} + HOCl \rightarrow HCl + \text{(oxidized and colorless molecule)}$$

Obviously neither wet chlorine nor HOCl will bleach a dye that cannot be oxidized. There are numerous dyes that are unaffected by chlorine bleaching materials.

5. Bleaching with Bleaching Powder. If a material to be bleached is first dipped into dilute H_2SO_4 solution and then into a suspension of bleaching powder, rapid bleaching occurs because HOCl is formed.

$$CaCl(OCl) + H_2SO_4 \rightarrow CaSO_4 + HCl + HOCl$$

Other acids may be substituted for H_2SO_4. Bleaching powder alone suspended in water will slowly cause bleaching because the CO_2 of the air dissolves in the water and forms carbonic acid which reacts with the bleaching powder, forming a slight amount of hypochlorous acid.

6. Bleaching and Disinfecting Preparations. Soluble hypochlorites, such as NaOCl, exert a slow bleaching action (much slower than with HOCl), and common bleaches such as Zonite, Clorox, and Javelle water usually contain sodium hypochlorite, or closely related substances. Solutions of this type possess powerful disinfecting properties and have found extensive use in sanitation and surgery. During the First World War, two eminent scientists (Carrel and Dakin) developed a solution containing sodium hypochlorite and sodium chloride, known as Carrel-Dakin solution, for the disinfection and irrigation of deep wounds. Had this solution been available during the Civil War, uncounted lives of soldiers would have been saved.

Bleaching powder, or chlorinated lime, can be used for sterilizing water and utensils used in handling milk and other foods, and water for domestic use. Because of mechanical difficulties in the use of bleaching powder, such as clogging of feed lines, it is now the usual practice to use chlorine from tanks in sterilizing the water supplied to cities.

7. War Gases. Chlorine may be regarded as both a blessing and a curse to mankind. We have just learned how it is used to sterilize water and to prevent infection in wounds. Unfortunately, men have found ways of making and using some of the very poisonous compounds of chlorine in warfare. Chlorine, first used by the Germans in France in 1915, was superseded by other more effective gases, mainly compounds of chlorine, some of which are listed in the accompanying table.

Common name	Formula	Chemical name
Phosgene	$COCl_2$	Carbonyl chloride
Mustard gas	$(C_2H_4)_2Cl_2S$	Dichlorodiethyl sulfide
Tear gas	CNO_2Cl_3	Chloropicrin or nitrochloroform (chloroform is $CHCl_3$)
Sneeze gas	$(C_6H_5)_2AsCl$	Diphenylchlorarsine

The possible use of war gases in the Second World War necessitated the large-scale manufacture and distribution of gas masks especially in Great Britain. The cannisters of gas masks contain charcoal and other substances known as *adsorbents*, specially prepared to adsorb the gases or neutralize their effects. Bleaching powder is an effective decontamination agent. New discoveries in the chemical warfare services in the different countries are, of course, closely guarded secrets. It is earnestly hoped that no nation will ever embark upon the widespread use of war gases. The secondary aftereffects of war gases may persist long after bullet or shrapnel wounds are healed.

Exercise

8. Review the formulas of the war gases listed in Sec. 7, and show by calculation which compound contains (*a*) the largest percentage, (*b*) the smallest percentage of combined chlorine.

8. Industrial Preparation of Chlorine. All large-scale production of chlorine is by the electrolysis of brine (VIII. 11).

Exercises

9. Write the equation for the electrolysis of brine.
10. Construct a labeled diagram of the cell used for the electrolysis of brine.

9. Laboratory Preparation of Chlorine, Oxidizing Agents. Chlorine may be conveniently prepared by the reaction of manganese dioxide or lead dioxide with hydrochloric acid. The gas is collected by upward displacement of air in a closed vessel under a laboratory hood, since it is heavier than air and soluble in water. The equations for the reactions are as follows:

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2 \qquad (1)$$

$$PbO_2 + 4HCl \rightarrow 2H_2O + PbCl_2 + Cl_2 \qquad (2)$$

It is to be noted that in the above equations two of the chloride ions of HCl are converted to Cl_2 gas and two of the chloride ions go to make up the chloride of the metal, also that the 4 hydrogen ions of HCl combine with the oxygen from the dioxide to form 2 molecules of water. As a general statement, we may say that the MnO_2 and the PbO_2 are oxidizing agents.

Other oxidizing agents, *e.g.*, potassium permanganate, $KMnO_4$, potassium dichromate, $K_2Cr_2O_7$, and potassium chlorate, $KClO_3$, also react with HCl, forming free chlorine. The HCl solution should be made by diluting concentrated HCl with water (about 1:1). The skeleton equations for these reactions are as follows:

$$KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + Cl_2 \qquad (3)$$

$$K_2Cr_2O_7 + HCl \rightarrow H_2O + KCl + CrCl_3 + Cl_2 \qquad (4)$$

$$KClO_3 + HCl \rightarrow H_2O + KCl + Cl_2 \qquad (5)$$

Exercises

11. Why is it incorrect to regard the MnO_2 as a catalytic agent in the reaction of MnO_2 with HCl?

12. Copy skeleton Eqs. (3) to (5) and balance each by estimating (*a*) the number of molecules of water formed, (*b*) the number of molecules of the chlorides formed, (*c*) the number of molecules of chlorine formed. (Note that in Eq. (3), 5Cl or $2\frac{1}{2}$ Cl_2 are formed in the balanced equation.)

Chlorine gas is also set free by the reaction of MnO_2 and other oxidizing agents, with a chloride salt mixed with dilute H_2SO_4. Such reactions are illustrated by the following balanced equations:

$$2NaCl + 3H_2SO_4 + MnO_2 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2 \qquad (6)$$

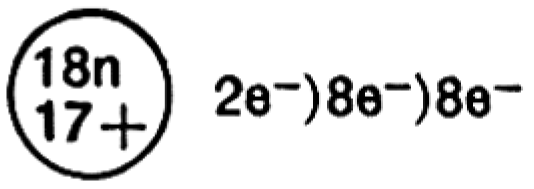
$$CaCl_2 + 2H_2SO_4 + MnO_2 \rightarrow CaSO_4 + MnSO_4 + 2H_2O + Cl_2 \qquad (7)$$

OXIDATION AND REDUCTION

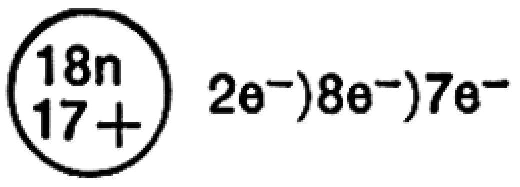
10. In each of the equations given in Sec. 9 we have noted that the oxidizing agent provides oxygen, which combines with H^+ of the acid, forming water. In this connection, then, we think of oxidation as combining with oxygen.

A more careful study of the foregoing equations, however, will reveal that a part of or all the chloride ions, Cl^-, are converted to free chlorine, Cl_2. In order to understand what is involved in this change, we shall review the structures of the ion and the atom of chlorine. (The atomic number of Cl is 17.)

The ion Cl^-



The atom Cl°



or

$17^+, 18e^-$ $\qquad$ $17^+, 17e^-$

When Cl^- is converted to Cl°, 1 electron is removed from the ion, thus,

$$Cl^- - 1e^- \rightarrow Cl^\circ$$

or

$$2Cl^- - 2e^- \rightarrow Cl_2$$

Loss or removal of electrons is called *oxidation.* Chloride ion is oxidized to chlorine.

Oxidizing agents (MnO_2, etc.) gain or combine with electrons and are thereby *reduced.* Gain of electrons is called *reduction.* The transfer, or gain and loss of electrons, is involved in all reactions of the oxidation-reduction type. The term *oxidation-reduction* has been extended to include all reactions that involve transference of electrons. Some of these reactions involve no oxygen at all, for example (see Exercise 4),

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \qquad (8)$$

This equation may be written in two steps, thus,

$$2I^- - 2e^- \rightarrow I_2 \qquad \text{(oxidation, loss } 2e^-\text{)}$$

or

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad \text{(reduction, gain } 2e^-\text{)}$$

Canceling the $2e^-$ and adding,

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Exercises

13. Which is the oxidizing agent and which is the reducing reagent in the above reaction?

14. For the reaction, $Zn + Cu^{++} \rightarrow Zn^{++} + Cu$, indicate (*a*) the electrons lost, (*b*) the electrons gained, (*c*) the substance oxidized, (*d*) the substance reduced.

15. Write another equation similar in type to that in Exercise 14 and answer the questions.

Relations exactly similar to the above are found in all oxidation-reduction reactions. It is to be remembered that

a. Oxidation is increase in the + valence of an element.

b. Reduction is decrease in the + valence of an element.

c. Oxidation involves loss of electrons.

d. Reduction involves gain of electrons.

e. Neither oxidation nor reduction ever occurs alone.

f. Total electrons lost always equal total gained.

g. The number of electrons gained or lost by a single atom is equal to its valence change.

h. Any element in the free state has a valence of zero.

The more important of these ideas are summarized in the following table:

Loss of electrons
Increase in positive valence
OXIDATION

$$\xrightarrow{\hspace{8em}}$$

(Valence numbers)

$$-3,\ -2,\ -1,\ 0,\ +1,\ +2,\ +3,\ +4,\ +5,\ +6,\ +7,\ +8.$$

$$\xleftarrow{\hspace{8em}}$$

Gain of electrons
Decrease in positive valence

REDUCTION

CHAPTER XII

THE HALOGEN FAMILY OF ELEMENTS

The group of elements, fluorine, chlorine, bromine, and iodine has been referred to as the halogen family of elements. The word *halogen* means "salt former." These elements are similar in many respects. Variations in properties, *e.g.*, color and physical state, occur in a regular manner with increasing atomic weight. These variations are summarized in Table I.

TABLE I

Halogen elements	Atomic weight	Color	Physical state at room temperature	Chemical activity	Halogen acids	Halogen salts
Fluorine.....	19	Very pale yellow	Gas	Most active	HF, hydrofluoric, very stable to heat; difficult to oxidize	Fluorides, NaF, CaF_2
Chlorine.....	35	Greenish yellow	Gas	......	HCl, hydrochloric	Chlorides, NaCl, $MgCl_2$
Bromine.....	79	Reddish brown	Liquid	......	HBr, hydrobromic	Bromides, NaBr, $MgBr_2$
Iodine.......	126	Purple	Solid	Least active	HI, hydriodic, decomposed easily by heat, easily oxidized	Iodides, NaI, KI

1. Occurrence. None of these elements occurs in the free state in nature, but their compounds are common. The most common compounds are CaF_2, NaCl, $MgCl_2$, NaBr, $MgBr_2$ (in brines and sea water), NaI, and $NaIO_3$ (sodium iodate found mixed with $NaNO_3$ in Chile saltpeter).

2. Uses. Some fluorides are used as insecticides and fungicides, others are used as fluxes in metallurgical operations. Hydrogen fluoride is used to etch glass. It is also an important catalyst. The compound, CCl_2F_2, dichlorodifluoromethane (Freon) is used extensively in refrigeration and in insecticide sprays. It is nontoxic to human beings and readily dissolves insecticide materials, *e.g.*, pyrethrum.

Bromine in the free state has no direct uses, but it is produced in appreciable amounts for the preparation of various useful bromides such as ethylene dibromide (a component of ethyl gasoline), silver bromide (the active material on a photographic film), and potassium bromide (a sedative in medicine).

Iodine is dissolved in alcohol to prepare *tincture of iodine.* A number of iodine compounds are of importance in medicine. Thus. potassium iodide is often used to cause absorption of blood clots in the eyes or in the brain. *Iodoform*, CHI_3, is used externally to reduce swelling and inflammation. A small amount of iodine is essential in the diet. Most of this iodine is concentrated in the thyroid gland which forms *thyroxin.* Apparently, a lack of sufficient thyroxin causes the serious degeneration known as *cretinism*, because administration of thyroxin is a successful method of treatment. The thyroxin used is extracted from the thyroid glands of sheep or may be synthesized in the laboratory.

Although there is a definite relationship between the amount of iodine taken into the system and the prevalence of goiter (disease of the thyroid gland), it is not to be concluded that lack of iodine is a universal cause of goiter. In older people, the exophthalmic type of goiter which is accompanied by protrusion of the eyeballs and serious heart and nervous disturbances may be due to an excess of thyroxin in the system. Individuals having symptoms of goiter should consult a medical specialist who will, in most cases, be able to relieve the difficulty by treatment or by surgery.

It is interesting to note that goiter is more prevalent in the inland regions of the United States than elsewhere, although this is not universally true; for example, the northern Pacific coastal region has a high goiter rate. Other factors such as elevation are involved. The lowest rate per thousand appears to exist in the areas along the Atlantic Coast and in the South Central states. Goiter is found about six times more frequently among women than among men.

3. Etching of Glass by Hydrogen Fluoride. Hydrogen fluoride is generally prepared by the reaction of H_2SO_4 with CaF_2. It is a gas and is very soluble in water, producing a weak acid.

$$HF \rightleftarrows H^+ + F^-$$

The formula of the gas is usually written H_2F_2. Experiments intended to establish this formula, however, show that the molecule varies in size (HF, H_2F_2, H_6F_6), depending upon the temperature. It is preferable to use the simple formula, HF, in equations that involve the ions.

Hydrofluoric acid must be kept in wax bottles because of its action on glass. Glass may be considered to be a mixture of Na_2SiO_3 and $CaSiO_3$. The reaction is shown by the equation:

$$\underset{\text{Calcium metasilicate}}{CaSiO_3} + 6HF \rightarrow \underset{\text{silicon tetrafluoride}}{SiF_4\uparrow} + 3H_2O + CaF_2$$

Exercises

1. Show by calculation that the percentage composition of each of the formulas HF, H_2F_2, and H_6F_6 is the same.
2. Write the equation for the reaction of CaF_2 and H_2SO_4 to produce HF.
3. Write equations for the reaction of HF (*a*) with Na_2SiO_3, (*b*) with SiO_2.

4. Displacement Series of the Halogens. Fluorine is the most active of the halogens and, when in the free state, it will displace any of the other halogens from a halide salt.

Chlorine stands next in activity after fluorine. Free chlorine will thus displace bromine from a bromide and iodine from an iodide, but not fluorine from a fluoride. Bromine is less active than chlorine but more active than iodine.

Exercises

4. Complete and balance the following if, and only if, the reaction will actually take place:

(*a*) $Cl_2 + KI \rightarrow$
(*b*) $Cl_2 + CaF_2 \rightarrow$
(*c*) $I_2 + KCl \rightarrow$
(*d*) $Br_2 + MgI_2 \rightarrow$
(*e*) $Br_2 + MgCl_2 \rightarrow$
(*f*) $Cl_2 + KBr \rightarrow$
(*g*) $I_2 + NaBr \rightarrow$
(*h*) $Cl_2 + HI \rightarrow$
(*i*) $Br_2 + HI \rightarrow$
(*j*) $I_2 + HCl \rightarrow$

5. Ionic Equations for Halogen Displacements. These equations may be written in exactly the same manner as in the case of the displacement of one metallic ion by another metal.

Exercises

5. Rewrite the equations of Exercise 4 (for each reaction that actually takes place) in the simplest possible ionic form. (Refer to XI. 10.)

6. Mark each of the equations of Exercise 5 to show the oxidation, reduction, and electrons gained and lost.

6. Preparation of the Halogens in the Free State. Fluorine may be prepared only by electrolysis of molten fluorides in copper apparatus. Chlorine is prepared either by electrolysis or by oxidation. Bromine and iodine are prepared either by electrolysis, oxidation, or displacement.

Exercises

7. Write equations to illustrate the two methods for the preparation of chlorine and the three methods for bromine.

8. Write equations for the electrolysis of water solutions of (*a*) KCl, (*b*) KBr, (*c*) KI. ($KCl + H_2O$, etc.)

9. Write equations for the following, assuming that the skeleton equations will be analogous to those for the preparation of chlorine:

$$KBr + MnO_2 + H_2SO_4 \rightarrow$$
$$KI + MnO_2 + H_2SO_4 \rightarrow$$

7. Stability of the Halogen Acids as Related to the Atomic Structure of the Halogens. In Table I it is stated that HF is very stable when heated and difficult to oxidize while HI decomposes when heated and is easily oxidized. Analogous properties are illustrated in the reactions of the halide salts with concentrated sulfuric acid. The *skeleton* equations for these reactions are as follows:

$$NaF + H_2SO_4 \rightarrow NaHSO_4 + HF$$
$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$$
$$HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$$
$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$$
$$HI + H_2SO_4 \rightarrow I_2 + H_2S + H_2O$$

It is an interesting scientific problem to explain the difference in reactions of the halogens and their compounds. Let us examine the atomic structure diagrams for the 4 atoms.

Element	Atomic number	Atomic structure	Atomic diameter, cm. × 10^8
F	9	$9^+)2e^-)7e^-$	1.28
Cl	17	$17^+)2e^-)8e^-)7e^-$	1.98
Br	35	$35^+)2e^-)8e^-)18e^-)7e^-$	2.28
I	53	$53^+)2e^-)8e^-)18e^-)18e^-)7e^-$	2.66

In fluorine there are only two electronic orbits (or levels) while in iodine there are five electronic orbits, outside of the nucleus. The outside orbit or valence orbit contains $7e^-$ in each case. To form the ions F^-, Cl^-, Br^-, I^-, requires the addition of one electron, $(1e^-)$ to the atom in each case; *e.g.*, $Cl + 1e^- \rightarrow Cl^-$, etc. According to the simple concept of electrical attraction of unlike (+ and −) charges, as related to radius or distance, it would be expected that the chlorine atom would attract an electron much more strongly than a bromine atom, and that the reaction,

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

would take place. Why?

By the same reasoning, we would expect that iodide ion, I^-, would lose its electron most readily and F^- the least readily of the group. Sulfur in concentrated H_2SO_4 has a strong attraction for electrons. Its structure may be expressed (for $H_2\overset{6+}{S}O_4$), as $16+)2e^-)\ 8e^-)$.

In the reactions of the halides with concentrated sulfuric acid, the sulfuric acid is an oxidizing agent (gains electrons) and the halide ions are, in the case of NaBr and NaI, reducing agents.

Exercises

10. Write atomic structures for the ions F^-, Cl^-, Br^-, I^-. For example, F, $9+)2e^-)8e^-$, etc.

11. Write the equation for the reaction of HBr with sulfuric acid, and balance it by indicating the correct numbers of electrons gained and lost. What is the oxidiation product? (The reduction product is SO_2.)

12. Repeat Exercise 11 for the reaction of HI with sulfuric acid. (The reduction product is H_2S.)

13. Explain why there is no oxidation and reduction in the reaction of NaF and NaCl with sulfuric acid.

8. Reactions of Halide Salts with Silver Nitrate. The soluble halide salts (chlorides, bromides, and iodides) form insoluble AgCl, AgBr, AgI, with silver nitrate solution.

Exercises

14. Tabulate the solubilities of AgF, AgCl, AgBr, AgI (see solubility table, Appendix) in grams per 100 cc. and in moles per liter of water.

15. Write (*a*) full ionic equations and (*b*) simple ionic equations for the reaction of $AgNO_3$ with NaCl; with KBr; and with MgI_2.

16. What industry makes use of such reactions on a large scale?

SUGGESTED READING

REINMUTH, Application of the Electronic Theory to Oxidation-Reduction, *J. Chem. Education*, **6**, 527 (1929).

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CHAPTER XIII

MOLECULAR WEIGHT AND VOLUME

The term *molecular weight* has been referred to in previous chapters. From the study of the crystal structure of electrovalent compounds, *e.g.*, sodium chloride, it is known that such compounds do not exist as separate and distinct molecules. The elements that make up these (solid) compounds exist as charged particles (ions) in definite positions in a continous pattern or lattice. It is therefore more appropriate to use the term *formula weight* rather than molecular weight in the case of these compounds. For example, the formula weight of sodium chloride, NaCl, is 58.45.

Compounds (and many of the gaseous elements) of the covalent type, however, do exist as separate and distinct molecules which have definite molecular weights. It is a comparatively simple operation to determine the molecular weight of such compounds, especially if they are liquids that can be easily vaporized, *e.g.*, benzene, carbon tetrachloride, and related compounds.

In this chapter, we shall consider some of the laws and principles upon which molecular weight determinations are based. Calculations involving relative volumes of gases, etc., will also receive attention. Some of these calculations are of great practical importance in the study of the combustion of fuels.

1. Relative Volumes of Gases in Chemical Reactions. In the demonstration of the electrolysis of water it was shown that 2 volumes of hydrogen and 1 volume of oxygen are formed. It can be shown also by experimental measurement (VI. 1) that, when hydrogen and oxygen are mixed in a closed tube and ignited by a spark forming steam (above 100°C.), the relative volumes of gases used and formed are

2 *volumes* hydrogen to 1 *volume* oxygen to 2 *volumes* steam

In the case of another well-known reaction, the combination of hydrogen with chlorine forming hydrogen chloride, the relative volumes are

1 *volume* hydrogen to 1 *volume* chlorine to 2 *volumes* hydrogen chloride

2. Gay-Lussac's Law of Combining Volumes. From a study of the two reactions referred to above and many other gaseous reactions, Gay-Lussac (1808) established the law of combining volumes: *At the same temperature and pressure, the relative volumes of gases used and formed in a reaction can be expresed as small whole numbers.* In Fig. 1, the application of this law to the reactions mentioned is shown in graphic form. In the application of this law, three important points are to be noted:

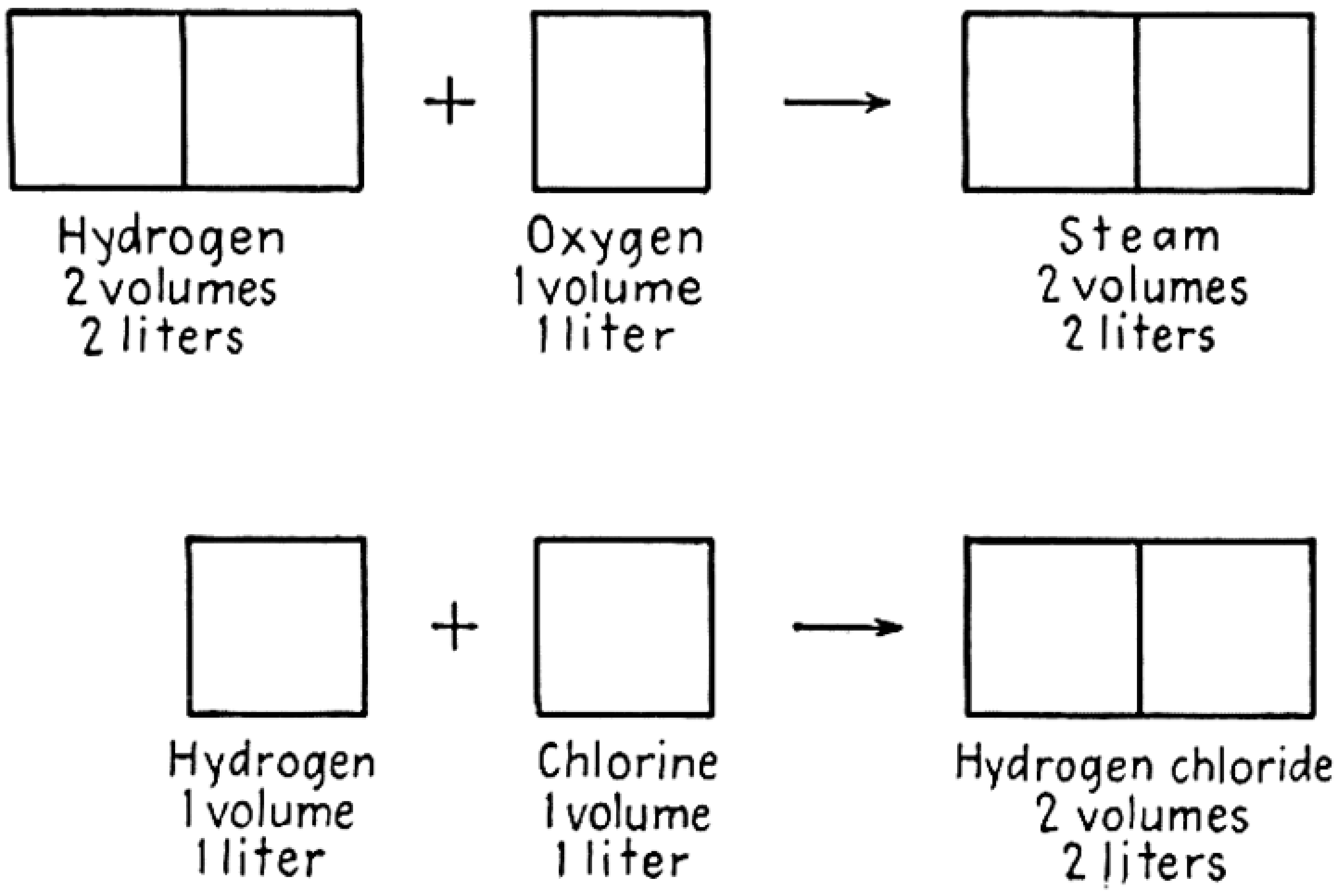

FIG. 1. Illustrations of Gay-Lussac's Law.

a. The total volumes of gases that react may be equal to, greater than, or less than the total volume of gases formed; *i.e.*, there may be contraction or expansion of the gases, owing to the fact that new products are formed in the reaction.

b. The total weight (mass) of the gases used always equals the total weight of the gases formed in the reaction, in conformity with the law of conservation of mass (II. 7).

c. The Gay-Lussac volume relations hold true only for gases (at the same temperature and pressure) and not for liquids and solids.

3. Avogadro's Law. Relation between Volumes and Molecules of Gases. Three years after Gay-Lussac's law was proposed, Avogadro, an Italian investigator, concluded (1811) that there must be some relationship between the relative volumes and the relative numbers of molecules involved in a gaseous reaction. This relationship first presented as a hypothesis and later known as Avogadro's law is stated as follows; *At the same temperature and pressure, equal volumes of all gases contain the same number of molecules.*

Avogadro's law explains a number of the properties of gases, *e.g.*, the uniform expansion of all gases with the same increase in temperature. By means of this law, the number of atoms in the molecule of oxygen, hydrogen, chlorine, etc., can be determined. The law is also a basis for the determination of molecular weights of gases and volatile liquids, and for calculations of relative densities and relative volumes of gases.

4. How Many Atoms in the Molecule of Oxygen and Other Gases? It has been shown that 2 volumes of hydrogen combine with 1 volume of oxygen, when ignited, forming 2 volumes of steam. From Avogadro's law it follows that 2 molecules of hydrogen combine with 1 molecule of oxygen forming 2 molecules of steam.

Hydrogen +	oxygen forms	steam	
2 volumes	1 volume	2 volumes	(by experiment)
2 molecules	1 molecule	2 molecules	(by Avogadro's law)

From the composition of steam, H_2O, we know that 2 molecules of steam contain 2 atoms of oxygen, which must come from the 1 molecule of oxygen. Therefore, 1 molecule of oxygen must contain 2 atoms of oxygen, O_2.

Exercises

1. Prove that there are 2 atoms of hydrogen in the molecule of hydrogen.

2. Prove that there are 2 atoms of chlorine in the molecule of chlorine. (Refer to the reaction of hydrogen with chlorine.)

5. Reacting Volumes of Gases. By means of Avogadro's law it is possible to calculate the relative volumes of gases used and formed in a gaseous reaction.

Exercises

3. (*a*) Balance the following equations and (*b*) indicate the relative volumes of gases used and formed in each reaction assuming that the temperature and the pressure remain constant:

(1) $CO + O_2 \rightarrow CO_2$
(2) $CH_4 + O_2 \rightarrow CO_2 + \underset{\text{steam}}{H_2O}$
(3) $C_7H_{16} + O_2 \rightarrow CO_2 + \underset{\text{steam}}{H_2O}$
(4) $\underset{\text{vapor}}{CS_2} + O_2 \rightarrow CO_2 + SO_2$
(5) $H_2S + O_2 \rightarrow SO_2 + \underset{\text{steam}}{H_2O}$

4. If 2 l. of (1) CO, (2) CH_4, (3) C_7H_{16}, (4) CS_2 (vapor), (5) H_2S are used in the respective reactions of Exercise 3, calculate for each reaction (*a*) the volume of oxygen required and (*b*) the volume of each product formed.

6. Gram Molecular Weight and Gram Molecular Volume. Since equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules and, since equal volumes of different gases have different weights (*e.g.*, at S.C., 1 l. of oxygen weighs 1.429 g. and 1 l. of hydrogen weighs 0.09 g.), it follows that these relative weights represent the relative weights of oxygen and hydrogen molecules.

By general agreement, chemists have adopted the weight of 22.4 l. of oxygen at S.C. (32 g.) as the standard basis for the determination of molecular weights of gases and volatile substances.

The *gram molecular weight* (G.M.W.) or the *mole* of a gas or a volatile substance is the weight of 22.4 l. at S.C. and the *gram molecular volume* (G.M.V.) of a gas or a volatile substance is the volume (22.4 l.) at S.C., occupied by 1 gram molecular weight of the substance. (The *pound molecular volume* or *pound mole volume* is 359 cu. ft. at S.C.) Table I contains these values for several common gases.

Table I

Gas	G.M.W., g.	G.M.V. (approximate), liters at S.C.
O_2	32	22.4
H_2	2.016	22.4
Cl_2	70.90	22.4
HCl	36.45	22.4
CO_2	44.01	22.4
SO_2	64.06	22.4
NH_3	17.024	22.4

From the data in Table I it is possible to calculate the weight of a given volume of any gas at S.C. (or at other temperatures and pressures).

Exercise

5. Calculate the weight of 1 l. of each of the following gases at S.C: O_2; Cl_2; CO_2; SO_2; NH_3. For example, for H_2,

$$22.4 \text{ l. } H_2 \text{ at S.C. weighs } 2.016 \text{ g.}$$

$$1 \text{ l. } H_2 \text{ at S.C. weighs } \frac{2.016}{22.4} = 0.09 \text{ g.}$$

7. How Many Molecules Are There in the Gram Molecular Weight or Gram Molecular Volume? Avogadro's Number. It has been determined by several experimental methods[1] that the actual number of molecules in the gram molecular weight or gram molecular volume is the enormous number, 6.02×10^{23}, or expressed in a more striking form, 602,000,000,000,000,000,000,000. This number, in honor of Avogadro, is called the *Avogadro number.* By means of this number one may calculate the actual weight of the single molecule. For example, the weight of the oxygen molecule is calculated as follows:

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[1] Sunier, "Some Methods of Determining Avogadro's Number." *J. Chem. Education*, 6, 299 (1929).

$$\frac{\text{G.M.W.}}{\text{Avogadro no.}} = \frac{32}{6.02 \times 10^{23}} = 5.3 \times 10^{-23} = \frac{5.3}{10^{23}}\text{ g.}$$

This value is, of course, far below the range of sensitivity of chemical balances, hence we must use the mole or gram molecular weight, 32 g. for oxygen, 36 g. for hydrogen chloride, etc., in work on molecular weights.

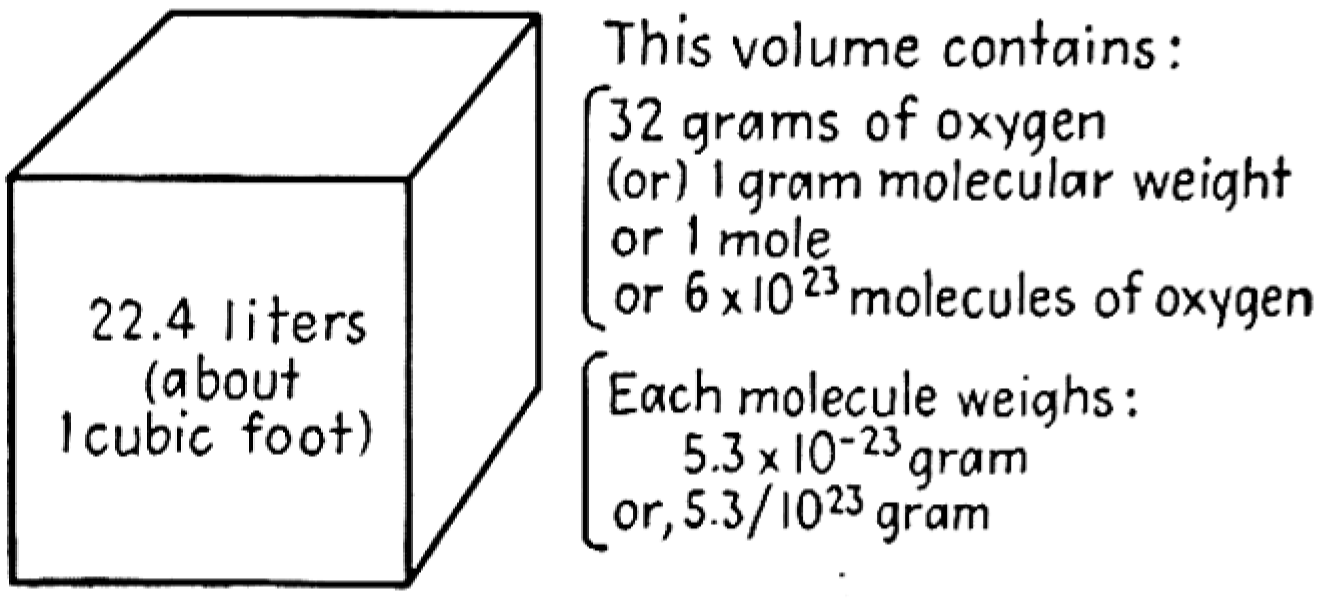
22.4 liters (about 1 cubic foot)
This volume contains:
32 grams of oxygen
(or) 1 gram molecular weight
or 1 mole
or 6×10^{23} molecules of oxygen
Each molecule weighs:
5.3×10^{-23} gram
or, $5.3/10^{23}$ gram

FIG. 2. The gram molecular volume.

Exercise

6. Calculate the weight of the single molecule of (*a*) Cl_2, (*b*) HCl, (*c*) CO_2, (*d*) SO_2, (*e*) H_2.

8. How Is Molecular Weight Determined? The gram molecular volume principle can be used to determine the molecular weight of a gas or a liquid that can be readily vaporized, the formula for which is not known. The weight of a measured volume of the vapor, at definite temperature and pressure, is found by experimental measurement.[1] From these values the molecular weight can be calculated.

Exercises

7. Calculate the molecular weight of a substance from the following data obtained in the laboratory: 269 ml. of the vapor measured at 99°C. and 740 mm. pressure weighs 1.35 g.

SUGGESTION: Calculate (*a*) the volume of the vapor in liters at S.C., (*b*) the weight in grams of 1 l., (*c*) the weight in grams of 22.4 l.

8. Given the following data: 1,280 ml. of a gas at 39°C. and 0.5 atm. pressure weighs 1.4 g. Calculate (*a*) the volume in liters at S.C. (*b*) the weight in grams of 1 l. at S.C., (*c*) the molecular weight of the gas.

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[1] An experiment on molecular weight determination should be performed by the student in the laboratory.

APPLICATIONS OF THE GRAM MOLECULAR WEIGHT AND GRAM MOLECULAR VOLUME PRINCIPLE

9. Relative Density and Specific Gravity of Gases. It is sometimes desirable to know whether one gas is heavier or lighter than another gas. To determine which of two gases is the heavier and in what ratio, one needs to compare only the molecular weights of the gases. The relative density of gases is defined as the relative weights of equal volumes of the gases at S.C.

Example. Calculate the relative density of chlorine and oxygen. (Refer to Table I for other illustrations.)

Calculation:

22.4 l. Cl_2 at S.C. weighs 70.9 g.
22.4 l. O_2 at S.C. weighs 32 g.

$$\frac{70.9}{32} = 2.2, \text{ relative density}$$

Therefore, chlorine is 2.2 times as heavy as oxygen.

The relative density of a gas compared to air is the specific gravity of a gas. Although air is a mixture of gases, we may use the weight of 22.4 l. air or 29 g., for comparison. (Why is this value, 29 g., not a true molecular weight?)

Example. Calculate the specific gravity of carbon dioxide, CO_2.

Calculation:

22.4 l. CO_2 at S.C. weighs 44 g.
22.4 l. air at S.C. weighs 29 g.

$$\frac{44}{29} = 1.53, \text{ the specific gravity of } CO_2$$

Exercise

9. Calculate (*a*) the relative densities of O_2 and H_2; of SO_2 and O_2, (*b*) the specific gravity of O_2, Cl_2, H_2.

10. Weight to Volume Calculations. Another useful application of the gram molecular weight and gram molecular volume principle is the calculation of the volume of a gas formed from a given weight of a reacting substance.

Example. Calculate the volume of oxygen at 30°C. and 740 mm. pressure that is set free by the decomposition of 20 g. potassium chlorate.

Calculation:

(1) Write the balanced equation for the reaction and assign the gram molecular weights and volume.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

2(122 g.) forms 3(22.4 l.) at S.C.

or

244 g. forms 67.2 l. at S.C.

(2) 244 g. $KClO_3$ forms 67.2 l. O_2 at S.C.

1 g. $KClO_3$ forms $\frac{67.2}{244}$ l. at S.C.

20 g. $KClO_3$ forms $20 \times \frac{67.2}{244}$ l. at S.C.

(3) Apply the temperature and pressure corrections.

$$20 \times \frac{67.2}{244} \times \frac{273 + 30}{273} \times \frac{760}{740} = 6.2,\ \text{l. } O_2$$

Exercises

10. Calculate the volume in liters of carbon dioxide at S.C. formed by the complete combustion of 120 g. carbon. (Give numerical statement and answer.)

11. Calculate the volume of hydrogen at 20°C. and 750 mm. pressure, set free by the electrolysis of 18 g. water. (Give numerical statement only.)

12. Calculate the volume in liters of hydrogen at 27°C. and 740 mm. pressure, set free by the reaction of 5.4 g. aluminum with an excess of sulfuric acid. (Give numerical statement only.)

11. Empirical and True Molecular Formula. If the percentage composition of a substance is known, it is possible to derive the *empirical formula,* or the simplest formula corresponding to this composition. The true molecular formula is the formula corresponding to the weight of 22.4 l. of the vapor of the substance at standard conditions. The molecular formula may be some multiple of the empirical formula.

Example. A hydrocarbon gas is known by analysis to contain 92.2 per cent carbon and 7.8 per cent hydrogen by weight. 120 ml. of this gas at S.C. weighed 0.1391 g. Calculate (*a*) the empirical formula, (*b*) the molecular weight, (*c*) the true molecular formula. The steps in the calculation are as follows:

(*a*) Empirical formula:

$$\frac{\%\ \text{carbon}}{\text{Atomic weight of carbon}} \text{ or } \frac{92.2\%}{12} = 7.68 \text{ atomic weights of carbon}$$

$$\frac{\%\ \text{hydrogen}}{\text{Atomic weight of hydrogen}} \text{ or } \frac{7.8\%}{1.008} = 7.74 \text{ atomic weights of hydrogen}$$

$$\frac{7.68}{7.74} = 0.99 \text{ or approximately 1 atomic weight of carbon}$$

$$\frac{7.74}{7.74} = 1.00 \text{ or 1 atomic weight of hydrogen}$$

Hence the empirical formula is C_1H_1 or CH.

(*b*) Molecular weight:

$$\begin{aligned}
120 \text{ ml. of the gas weighs } & 0.1391 \text{ g.} \\
1 \text{ ml. of the gas weighs } & \frac{0.1391}{120} \text{ g.} \\
1{,}000 \text{ ml. or } 1 \text{ l. weighs } & 1{,}000 \times \frac{0.1391}{120} \text{ g.} \\
22.4 \text{ l. weighs } & 22.4 \times 1{,}000 \times \frac{0.1391}{120} = 26 \text{ g}
\end{aligned}$$

Therefore the molecular weight is 26.

(*c*) True molecular formula:
The weight of the empirical formula, CH, is $12 + 1 = 13$.

$$\frac{\text{True molecular weight}}{\text{Empirical molecular weight}} \text{ or } \frac{26}{13} = 2$$

Hence,

$$2(CH) = C_2H_2$$

The true molecular formula, then, is C_2H_2 (not CH, or C_3H_3, or C_4H_4, etc.).

Exercise

13. A gas has the following composition; carbon 85.7 per cent; hydrogen 14.3 per cent. One liter of the gas at S.C. weighs 1.875 g. Calculate (*a*) the empirical formula, (*b*) the molecular weight, (*c*) the true molecular formula.

CHAPTER XIV

SULFUR AND HYDROGEN SULFIDE

SULFUR

Among the solid nonmetallic elements, sulfur holds a very prominent position, as to both the abundance of its natural deposits and the many uses of sulfur and its compounds in agriculture and industry.

1. Industrial Importance and Uses. Sulfur is produced in great quantities (several million tons yearly) because of its many uses. By far the largest use of sulfur is for conversion into sulfur dioxide, which in turn is converted largely into calcium bisulfite and sulfuric acid. The uses of these three substances are indicated in a following section.

Large amounts of sulfur are used directly in vulcanization of rubber, as a fungicide especially in vineyards, and in making lime sulfur spray, as well as in fertilizer mixtures, in gunpowder, dyestuffs, fireworks, and cements, and more recently in special lubricants. Lime sulfur sprays contain polysulfides of calcium, CaS_x, *e.g.*, CaS_5. The sulfur mixed with phosphate rock fertilizers probably is slowly converted to sulfuric acid, which converts the phosphate to a form more readily available to the plant.

Exercise

1. What property of sulfur makes it useful in fireworks and gunpowder?

In cements, sulfur is useful because of its low melting point and because of the inertness and excellent insulating quality of the solid. In lubricants, sulfur is used by being dissolved or suspended in an oil. Such lubricants are useful in machining operations where the tools and work become very hot because the sulfur retains its viscosity and lubricating effect.

Smaller quantities of sulfur are converted into sulfur monochloride, S_2Cl_2, for use in vulcanizing rubber; into phosphorus trisulfide, P_4S_3, and antimony trisulfide, Sb_2S_3, for use in matches because these compounds ignite easily and are readily combustible; and into carbon disulfide which is used in large quantities in the manufacture of rayon and also as an insecticide and rodent eradicator. As carbon disulfide is very inflammable and forms explosive mixtures with air, it must always be used with complete precautions to avoid sparks or open flame.

The smelting of copper, lead, nickel, and similar ores produces large quantities of sulfur dioxide as a by-product. Recently constructed plants are equipped to recover this gas by conversion to sulfuric acid. Older plants not so equipped allowed sulfur dioxide fumes to destroy surrounding vegetation. Sulfur is also recovered as a by-product during the purification of manufactured fuel gas.

The sulfur content of coal, gasoline, and fuel oil is important because, during combustion of the fuel, the sulfur is at least partly converted to sulfurous acid or sulfuric acid, which in time causes serious corrosion of any metal parts exposed to the combustion gases. Steel must be almost entirely free of sulfur; consequently, iron ores low in sulfur content are always preferred by iron- and steelmakers.

2. Occurrence of Sulfur in Nature. Free sulfur occurs in large quantities in certain strata as much as 1,000 ft. below the surface in Louisiana and Texas near the Gulf of Mexico. These deposits are the chief source of commercial sulfur at present. Sulfur is also found in the free state in volcanic and hot spring regions. In Italy such sulfur deposits are worked commercially.

Sulfur also occurs naturally in large amounts in the form of metallic sulfides. Important among these are mercury sulfide (cinnabar, HgS), zinc sulfide (sphalerite, ZnS), lead sulfide (galena, PbS), copper sulfide (chalcocite, Cu_2S), and chalcopyrite, $CuFeS_2$. These ores are used as important sources of the respective metals Hg, Zn, Pb, Cu. Galena has been used as a detector crystal in radio sets. Sphalerite is sometimes used as a source of sulfur dioxide as well as zinc. Iron pyrites or fool's gold, FeS_2, occurs naturally in the form of crystals and is often used as a source of sulfur dioxide, but not as a source of iron because of the fact that it is not economically feasible to extract the iron.

Gypsum, the dihydrate of calcium sulfate, is a compound plentiful in many parts of the world. It is found associated with the sulfur deposits of Louisiana and Texas. One theory assumes that microorganisms converted some of the gypsum to sulfur during past ages. Anhydrite or anhydrous calcium sulfate is also a common mineral. Many other sulfides and sulfates are found in natural deposits.

3. Frasch Process for Extracting Sulfur from the Earth. Sulfur melts readily in superheated water and steam (at 114°C.). When compressed air is blown into a mixture of melted sulfur and hot water, the mixture becomes like a froth and can readily be forced through pipes. These properties were utilized by Herman Frasch, an American engineer, who (about 1900) developed the well-known process, named for him. In this process, the sulfur is forced upward from the deposits several hundred feet below the surface by means of three concentric pipes sunk in a well (Fig. 1). Superheated water passes downward through the outer pipe and compressed air is forced downward through a small central pipe. Molten sulfur mixed with air and water passes upward through the second one of the three pipes. This mixture is conducted to huge bins where it soon forms solid sulfur. The walls of the bins are then removed, and the sulfur is broken down by means of dynamite. It is then ready for shipment. Since 1905, practically all of the sulfur used in the United States has come from the deposits in Louisiana and Texas. In 1940, the United States produced nearly 3,000,000 tons of sulfur. According to present estimates, there are sufficient reserves to meet the demands for the next 40 years.

4. Allotropic Forms of Sulfur and Their Physical Properties. The most common form of sulfur (the rhombic form) is a hard, yellow, brittle solid, insoluble in water, soluble in carbon disulfide, melting a little above the boiling point of water, and being a nonconductor of heat and electricity.

Sulfur occurs in two solid crystalline forms, one amorphous solid or plastic form, two liquid forms, and several vapor forms. All forms have identical chemical properties but different physical properties. At room temperature, rhombic sulfur is the stable form, all other forms changing into this form in time. Ordinary powdered sulfur, flowers of sulfur, and solid lumps of sulfur (roll sulfur) are composed of innumerable small rhombic crystals.

If rhombic sulfur is heated above 96°C., it is converted to monoclinic sulfur; if the latter is cooled below 96°C., it slowly reverts to the rhombic form. This temperature is known as the *transition point.*

The melting point of sulfur is 114°C. The liquid sulfur consists of a mixture of two liquid forms: lambda sulfur, $S\lambda$, and mu sulfur, $S\mu$. This property results in at least two peculiarities of liquid sulfur: (1) The actual melting point depends upon the relative amounts of the two forms, so that the melting point or freezing point of sulfur varies with the previous treatment of the sample. (2) Although liquid sulfur just above its melting point (around 114°C.) is quite fluid, it becomes increasingly viscous as its temperature is increased, until at about 250°C. a test tube of liquid sulfur can be inverted without the loss of sulfur. This behavior arises because $S\lambda$ is quite fluid but

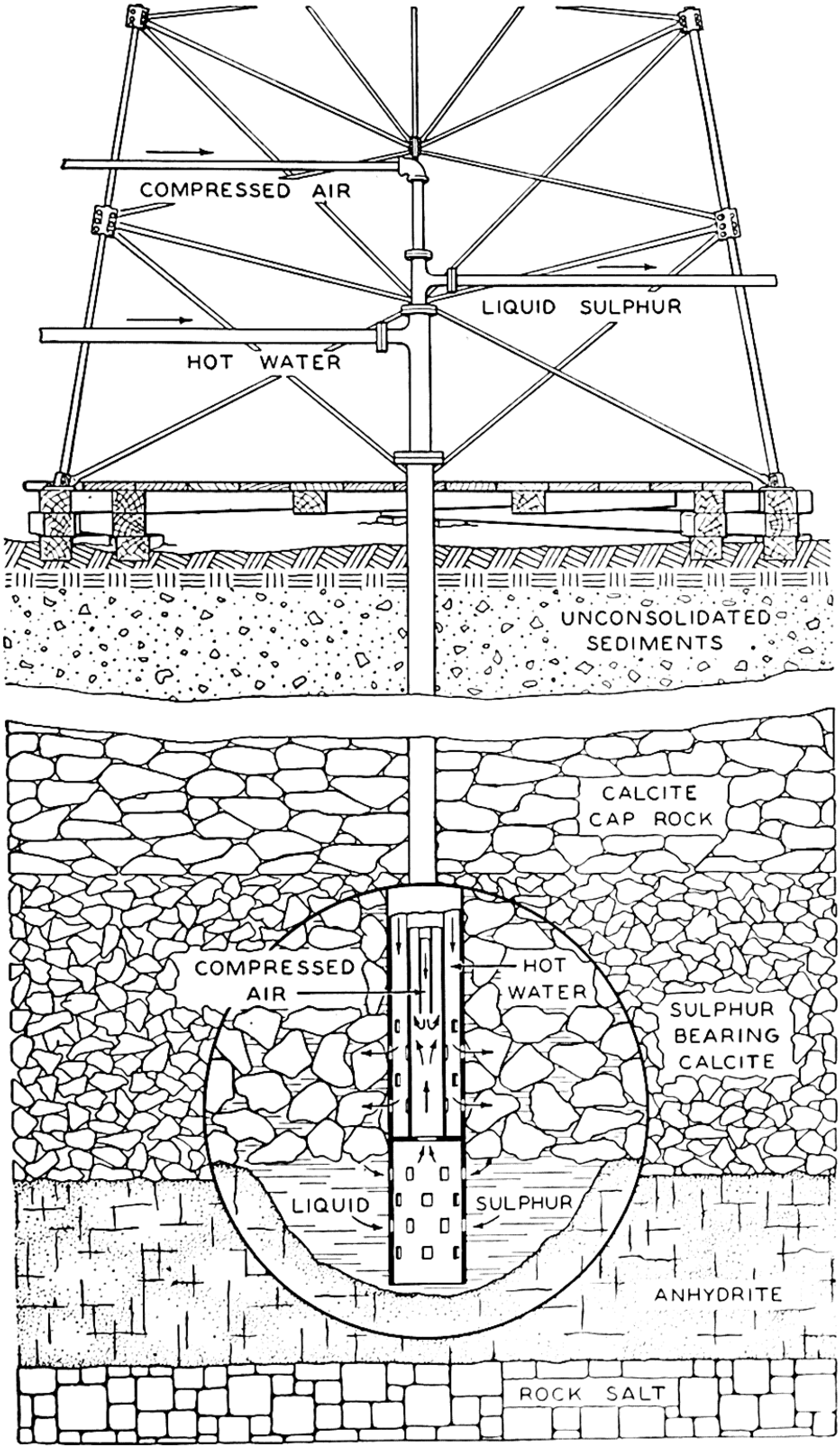


FIG. 1. Sulfur well piping. (*Texas Gulf Sulphur Co., Inc.*)

changes into Sμ on being heated. The latter is a very viscous material at all temperatures below 300°C.

5. Chemical Properties of Sulfur. Sulfur, like oxygen, although relatively inactive when cold, unites with a great many other elements when hot. Most of these reactions liberate considerable heat and so continue of their own accord once the reaction has been well started, forming sulfides.

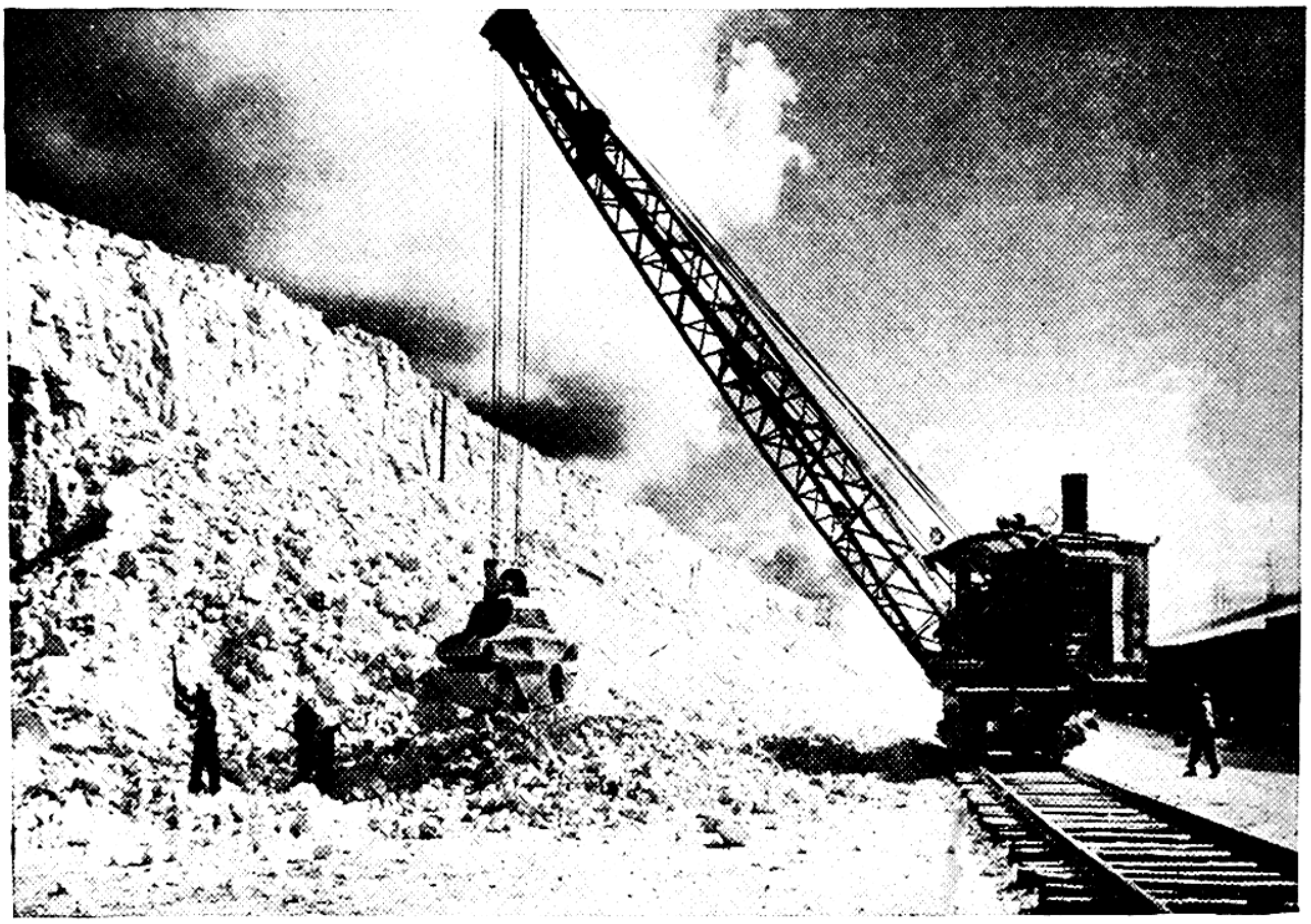


FIG. 2. Sulfur ready for loading. (*Texas Gulf Sulphur Co., Inc.*)

Exercise

2. Write equations for the reaction of sulfur with oxygen, iron, silver, copper, and carbon.

Even at room temperature, sulfur tarnishes most metals because a surface layer of metallic sulfide is formed. Sulfur is very slowly converted to sulfuric acid by the oxygen and moisture of ordinary air. This property is applied in the use of sulfur in phosphate fertilizer mixtures.

HYDROGEN SULFIDE AND OTHER SULFIDES

6. Occurrence and Physical Properties. Hydrogen sulfide, H_2S, is a colorless gas with a very disagreeable odor. It is found in certain springs (sulfur water). In the decomposition of protein materials, *e.g.*, eggs, the combined sulfur in the protein is converted into hydrogen sulfide, thus accounting for the disagreeable odor of decayed eggs, meat, and other protein foods. Hydrogen sulfide is poisonous if breathed in large concentrations for any length of time.

7. Preparation. Hydrogen sulfide may be prepared by the direct combination of hydrogen with hot sulfur or by the reaction of metallic sulfides with hydrochloric or sulfuric acid according to the following reactions:

$$H_2 + S \rightarrow H_2S$$
$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

Exercise

3. Calculate the volume of H_2S measured at 20°C. and 745 mm. pressure, produced by the reaction of 25 g. ferrous sulfide, FeS, with an excess of HCl.

8. Chemical Properties of Hydrogen Sulfide. Hydrogen sulfide is a weak acid, forms two series of salts (normal and acid or hydrosulfides), and is a good precipitating agent for many metallic ions. It is unstable toward heat, is a good reducing agent, and is readily combustible. Hydrogen sulfide tarnishes most metals, owing to the formation of a surface film of metallic sulfide. This reaction is most familiar in the case of silver. The ionization of hydrogen sulfide in solution takes place in two stages:

$$H_2S \rightleftarrows H^+ + HS^- \qquad \text{(hydrosulfide ion)}$$
$$HS^- \rightleftarrows H^+ + S^{--} \qquad \text{(sulfide ion)}$$

Exercises

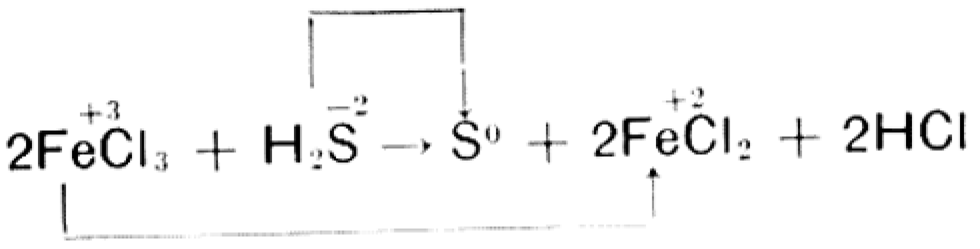
4. Write molecular and ionic equations for the formation of (*a*) sodium hydrosulfide, (*b*) normal sodium sulfide, (*c*) calcium hydrosulfide, (*d*) normal zinc sulfide, (*e*) normal ammonium sulfide.

5. Write molecular and ionic equations for the precipitation of the following sulfides: (*a*) HgS, (*b*) PbS, (*c*) Ag_2S, (*d*) As_2S_3, (*e*) SnS_2.

6. Write an equation for the effect of heat on H_2S. This reaction is called *cracking* of H_2S.

Hydrogen sulfide reduces many other substances. In this process the sulfide ion of the H_2S is oxidized, forming a finely divided white or pale yellow precipitate, which settles very slowly and is sometimes called *milk of sulfur*.

When H_2S is allowed to react with ferric chloride solution, the following reaction takes place:



$$2\overset{+3}{Fe}Cl_3 + H_2\overset{-2}{S} \rightarrow S^0 + 2\overset{+2}{Fe}Cl_2 + 2HCl$$

Exercises

7. Label the above equation to show oxidation and reduction, also gain and loss of electrons.

8. Write similar equations for the reaction of H_2S with (*a*) ferric sulfate, (*b*) iodine, (*c*) sulfur dioxide. Label in each case to show oxidation, reduction, gain and loss of electrons.

9. Write a similar equation for the reaction of oxygen with H_2S. This reaction may be brought about by simply bubbling oxygen (or air) through a solution of hydrogen sulfide. It occurs slowly if such a solution is merely allowed to stand exposed to air.

When hydrogen sulfide burns with an excess of air or oxygen, the products are water and sulfur dioxide (complete combustion). If oxygen is deficient, sulfur and water are formed (incomplete combustion), or partial cracking may occur.

Exercises

10. Write equations for the complete and incomplete combustion of hydrogen sulfide.

11. What volume of oxygen at S.C. would be required to burn 1,200 cc. H_2S to SO_2?

12. What volume of SO_2 at S.C. will be formed when 500 cc. H_2S is burned with oxygen to form SO_2 and H_2O?

13. What volume of H_2S at S.C. could be burned to SO_2 with 100 l. O_2?

14. What volume of H_2S at S.C. would have to be burned to form 10 l. SO_2?

15. What volumes of H_2S and of O_2 at S.C. will react to form 1,000 cu ft. SO_2?

9. Test for Hydrogen Sulfide Gas. Filter paper is wet with lead acetate, $Pb(C_2H_3O_2)_2$, solution, and this lead acetate paper immediately turns black when placed in an atmosphere containing even a minute percentage of hydrogen sulfide. Why?

Exercise

16. Write the equation for the above reaction.

10. Tests for Sulfide Salts. Many but not all sulfide salts react with dilute HCl or H_2SO_4 with evolution of H_2S, which can be detected as above indicated, if not by its odor.

Exercise

17. Write equations for the reaction of (*a*) HCl, (*b*) H_2SO_4, with each of the following: FeS, MnS, ZnS, $Ca(HS)_2$, Na_2S.

11. Use of Hydrogen Sulfide in Analysis. Hydrogen sulfide may be used to identify a number of metallic ions in solutions of their salts because the sulfides have characteristic colors and also characteritsic solubilities in acids. The latter properties also make it possible to separate metallic sulfides from one another by using an acid that dissolves one sulfide but does not dissolve some other sulfide.

12. Polysulfides and Persulfides. Many sulfides are known in which more than the normal proportion of sulfur is present. Sodium sulfide solution will dissolve a considerable excess of sulfur. The resulting solution contains polysulfides or persulfides of sodium, such as Na_2S or Na_2S_4, and is generally assigned the formula Na_2S_x. Ammonium polysulfide $(NH_4)_2S_x$, essentially $(NH_4)_2S_2$, calcium persulfides, CaS_4, CaS_5 are other well-known examples.

CHAPTER XV

OXIDES AND ACIDS OF SULFUR

In our study of oxygen we learned that sulfur burns readily, forming sulfur dioxide. In this chapter we shall consider methods by which sulfur dioxide is converted to sulfuric acid, a compound of great importance in the chemical industry. Other related compounds of sulfur will also be described.

1. General. There are two common oxides of sulfur: the dioxide, SO_2, and the trioxide, SO_3; and three common acids: sulfurous, H_2SO_3, sulfuric, H_2SO_4, and pyrosulfuric or fuming sulfuric, $H_2S_2O_7$. The salts of the first two acids are quite common. Each acid forms two series of salts: the normal and the acid salts.

All *normal sulfites* have the radical SO_3 with valence of -2; *normal sulfates* have the radical SO_4 with valence -2. All *acid sulfites* (*bisulfites*) have the radical HSO_3, valence -1; *bisulfates* have the radical HSO_4, valence -1.

Exercise

1. Tabulate the formulas for the normal and acid sulfates and sulfites of (*a*) sodium, (*b*) calcium, (*c*) zinc.

2. Sulfur Dioxide, Preparation and Properties. Sulfur dioxide is formed when any sulfite is acted upon by an acid. It is also formed when the less active metals are allowed to react with hot concentrated sulfuric acid.

It is a colorless gas with a very suffocating odor, which induces coughing when inhaled for a short time. The gas can be liquefied at a slight pressure, at room temperature, and the liquid boils at $-10°C.$ at 1 atm. of pressure. Approximately 40 volumes of sulfur dioxide dissolve in 1 volume of water, at ordinary conditions, forming sulfurous acid, H_2SO_3.

Exercises

2. Write equations for the reactions of three different sulfites with two different acids.

3. Write equations for the reaction of hot concentrated sulfuric acid with (*a*) copper, (*b*) mercury ($HgSO_4$ is formed), (*c*) silver.

4. What volume of oxygen is needed to form 450 cc. of SO_2 by "roasting" ZnS? (ZnO is formed.) (All gases at S.C.)

5. What volume of SO_2 could be formed by roasting FeS_2 with 10,000 cu. ft. of oxygen? (Fe_2O_3 is formed.) (All gases at S.C.)

6. What volume of SO_2 could be formed by roasting FeS_2 with 10,000 cu. ft. of air? (All gases at S.C.) (Air contains about 20 per cent O_2 by volume.)

3. Uses of Sulfur Dioxide. The largest uses are in the manufacturing of sulfuric acid and the preparation of calcium bisulfite, $Ca(HSO_3)_2$, solution which is employed in large quantities in the paper industry because, when wood chips are heated with it, they are disintegrated into pulp. Colored and resinous substances in the wood are largely removed or destroyed.

Sulfur dioxide itself has been used in household refrigerators because it is liquefied by a relatively low pressure. Sulfur dioxide is also an important bleaching agent for silk, hair, wool, feathers, straw, and fruit. It bleaches these materials without harming the materials themselves. Its use on dried fruits is not only to prevent dark-colored substances from forming but also to act as a fungicide. Some liquid sulfur dioxide is used to extract undesirable components from lubricating oil and thus improve its quality.

4. Chemical Properties of Sulfur Dioxide and Sulfurous Acid. Sulfur dioxide unites readily with water to form sulfurous acid.

$$H_2O + SO_2 \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$$

Sulfurous acid is a weak acid and is also unstable toward heat. Even at room temperature sulfurous acid is considerably decomposed into SO_2 and H_2O; at higher temperatures it is completely decomposed. Sulfurous acid is a reducing agent as illustrated by its reaction with oxygen and with iodine in water.

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4 \qquad \text{(very slow action)}$$
$$H_2SO_3 + I_2 + H_2O \rightarrow 2HI + H_2SO_4$$

Exercise

7. Indicate the valence changes and the oxidation and reduction in each of the above equations.

5. Manufacture of Sulfuric Acid. This is done by two methods, the *chamber process* and the *contact process*. Both of these processes are catalytic in nature. In the case of the chamber process the exact reactions are quite complicated. Table I gives the outstanding characteristics of the two processes.

TABLE I

	Chamber Process	*Contact Process*
Starting materials:	SO_2, O_2 (air) H_2O (steam)	SO_2, O_2 (air) H_2O (water) Some conc. H_2SO_4
Catalyst:	Oxides of nitrogen	Finely divided platinum, or vanadium pentoxide, V_2O_5.
Reactions (simplified):	(1) $SO_2 + NO_2 \rightarrow SO_3 + NO$ (2) $SO_3 + \underset{\text{steam}}{H_2O} \rightarrow H_2SO_4$ (3) $2NO + \underset{\text{air}}{O_2} \rightarrow 2NO_2$	(1) $2SO_2 + O_2 \xrightarrow{[Pt]} 2SO_3$ (2) $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (3) $\underset{\substack{\text{pyrosulfuric}\\ \text{acid}}}{H_2S_2O_7} + H_2O \rightarrow 2H_2SO_4$
Product:	Approx. 60% H_2SO_4	Approx. 100% H_2SO_4
Chief expense:	Lead chambers Repairs Replacing oxides of N	Catalyst Purification of SO_2

In the chamber process the starting materials and oxides of nitrogen are passed into large lead chambers (often about 50 ft. square and equally high). The oxides of nitrogen are recovered and reintroduced into the chambers, and the dilute sulfuric acid is concentrated by the same series of ingenious processes. There is considerable evidence that the actual reactions are more complicated than is indicated above, but the final result is the same as if reactions (1), (2), and (3) took place in the chambers.

In the contact process it is absolutely essential to purify the sulfur dioxide because even slight traces of impurities (such as arsenic compounds) destroy the activity of the catalyst. Oxides of vanadium are quite frequently used as catalysts instead of platinum. The mixture of sulfur dioxide and air is passed through a tube containing the catalyst, and the resulting gas is passed into concentrated sulfuric acid. Pyrosulfuric (fuming sulfuric) acid or *oleum* is formed and, later, sufficient water is added to convert this to 100 per cent sulfuric acid. It is not practical to pass the SO_3 directly into water because it is not readily absorbed in water.

Exercises

8. 10 l. SO_2 are passed over a platinum catalyst with 10 l. oxygen. What are the volumes of the different gases coming out of the catalyst tube? (Assume 100 per cent conversion.)

9. 12 l. SO_3 would require what volumes of sulfur dioxide and oxygen for its formation?

10. 12 l. SO_2 and 10 l. air (20 per cent O_2, 80 per cent N_2) are passed over a platinum catalyst as in the contact process. What are the volumes of the different gases coming out of the catalyst tube?

6. Uses of Sulfuric Acid. Sulfuric acid is produced to the amount of 10 or more million tons yearly. Especially large uses are the production of superphosphate and ammonium sulfate fertilizers, the destruction of gums and resins in gasoline and other petroleum products, the cleaning of steel and other metals before galvanizing or tinning, as well as in storage batteries and electroplating, also in explosives and nitrocellulose manufacture. Of course various sulfate salts, such as $CuSO_4$, $FeSO_4$, and $Al_2(SO_4)_3$, are made by using H_2SO_4 as a starting material. A great many other chemicals also require it for their preparation. The sales of sulfuric acid at any time in any region are an excellent index as to general business activity, because the uses of sulfuric acid are so numerous and so widely distributed through various industries.

7. Physical and Chemical Properties of Sulfuric Acid. Pure sulfuric acid is an oily liquid about 1.8 times as heavy as water. Its chemical properties may be summarized by stating that it is an active acid, an excellent dehydrating agent, and also an oxidizing agent especially when hot and concentrated.

Exercises

11. Write the equation for the ionization, in steps, of H_2SO_4.

12. Write molecular and ionic equations for the formation of the following salts by neutralization: (*a*) normal sodium sulfate, (*b*) ammonium bisulfate, (*c*) zinc sulfate, (*d*) ferric sulfate.

13. Write an equation for the dehydrating action of sulfuric acid, on sugar, $C_{12}H_{22}O_{11}$. (Carbon is formed.)

14. Write an equation to illustrate the oxidizing action of sulfuric acid (*a*) with copper, (*b*) with carbon.

8. Sodium Thiosulfate. If a solution of sodium sulfite is boiled with sulfur, sodium thiosulfate, $Na_2S_2O_3$ (hypo), is formed. This is a white solid, very soluble in water. Its solution has the property of dissolving silver bromide and is therefore used to "fix" photographs.

When $Na_2S_2O_3$ solution is acidified, a slowly settling precipitate of finely divided sulfur is formed, and SO_2 gas is evolved.

$$Na_2S_2O_3 + H_2SO_4 \rightarrow H_2O + SO_2\uparrow + S\downarrow + Na_2SO_4$$

9. Tests for Sulfate, Sulfite, and Thiosulfate Salts. These are summarized in Table II, which assumes familiarity with three common testing procedures.

TABLE II

Reagent	Sulfate	Sulfite	Thiosulfate
$BaCl_2$ HCl test	White ppt. of $BaSO_4$ unchanged by HCl	White ppt. of $BaSO_3$ dissolved by HCl with $SO_2\uparrow$	May or may not form white ppt. with $BaCl_2$. Addition of HCl will cause formation of finely divided, often white sulfur and $SO_2\uparrow$
$AgNO_3$ HNO_3	Usually no ppt. White ppt. sometimes forms but is easily soluble in HNO_3	Almost always forms a white ppt., Ag_2SO_3, which is difficult to dissolve in HNO_3	Always forms a white or yellow ppt. of $Ag_2S_2O_3$ that rapidly turns brown and then black. Very characteristic
Dilute H_2SO_4 on solid salt	No action except that salt may dissolve	SO_2 gas evolved. Salt dissolves to clear solution	SO_2 gas evolved; finely divided white or yellow sulfur forms slowly in solution

Exercise

15. Identify the salts containing sulfur which gave the following tests: Salt No. 1. When treated with HCl formed sulfur dioxide and a precipitate of sulfur. Salt No. 2. When $BaCl_2$ was added to a water solution of the salt, a white precipitate was formed which dissolved in HCl, forming SO_2.

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CHAPTER XVI

CLASSIFICATION OF THE ELEMENTS

In the study of the halogen family of elements (Chap. XII), it was shown that these elements (fluorine, chlorine, bromine, and iodine) exhibit a definite gradation in their properties. For example, with increase in atomic weight, there is a corresponding change in state as indicated in Table I.

TABLE I
HALOGEN FAMILY OF ELEMENTS

Element	Atomic weight	Physical state
Fluorine..................	19.0	Light-yellow gas
Chlorine..................	35.45	Greenish-yellow gas
Bromine..................	79.9	Reddish-brown liquid
Iodine.....................	126.9	Dark-gray solid

The valence numbers and chemical properties are so closely related that the term *family* is used in referring to the group. We shall, presently, take up the study of other families of elements, and their similarities will be described.

1. Classification of Elements. Chemists have been studying the problem of classifying the elements for more than 100 years. From the investigations of Döbereiner, Newlands, Mendelyeev,[1] and others, we now have a chart or table which classifies all the elements in the order of their increasing atomic weight. The chart shown in Table II is known as the *Mendelyeev periodic system* because Mendelyeev (1872) included all the elements known at that time and pointed out the great value of the system in predicting other elements and reactions hitherto unknown. There were numerous gaps in this early table, which have been filled in as these elements have been discovered.

Other chemists, *e.g.*, Soddy of England and Harkins of the United States, have constructed systems based upon space models, which have certain advantages. Moseley of England, in 1911, worked out a system of the elements based upon their atomic numbers, which appears to be the most exact classification known.

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[1] The original Russian name, Mendelejeff, is pronounced as indicated by the word, Mendelyeev; hence the latter spelling is adopted in this book.

2. The Periodic Table. Although the Mendelyeev system has certain irregularities, it is very helpful in the study of chemical properties and we shall now examine it in some detail.

Families or Groups. It will be observed that the halogen family is in the vertical column indicated as Group VII. Note that the atomic weights are placed under the respective elements. (The atomic numbers are shown above the elements.) The type formula, E_2O_7, represents the composition of the higher oxides and the formula, EH, represents the hydrogen compounds, HCl, HBr, etc. In this group, the maximum positive valence is seven and the negative valence is one. In general, the group number represents the positive valence of the elements of that family, although there are certain exceptions to this rule. For example, iron, cobalt, and nickel, in Group VIII, have valence numbers of two and three in their respective compounds.

In Group 0, at the left of the table, we find the inert gases, helium, neon, argon, krypton, xenon, and radon which have the valence number zero, because they form no compounds. Group I contains the alkali metals, lithium, sodium, potassium, rubidium, and cesium. The valence number is one in all their compounds.

Subgroups. The metals, copper, silver, and gold, also found in Group I, are related to each other but are not so closely related to the alkali metals. These metals comprise what is known as subgroup IB. There are two subgroups in Group II: the IIA group comprising the alkaline earth metals, calcium, strontium, barium (and radium) and the IIB group comprising zinc, cadmium, and mercury. The same situation is met with in the other groups. In some cases, the elements have variable valence numbers. For example, copper and mercury have valence numbers of both one and two in their various compounds.

In regard to families or groups of elements, it is to be noted that, as we pass downward in a group from one element to the next, the metallic character of the elements becomes more pronounced with increasing atomic weight, or the properties become increasingly less nonmetallic in type, as in the case of the halogen family.

Series. We shall now consider some of the relationships of the horizontal rows or series of the elements. If, for example, we start in Series 2 with helium and pass in succession the seven elements, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine arranged in the order of increasing atomic weight, we find the eighth element, neon, in Series 3, Group 0, under helium which it resembles closely. In

TABLE II

PERIODIC CLASSIFICATION OF THE ELEMENTS (MENDELYEEV PLAN)

(Atomic numbers above symbols; atomic weights below symbols)

Series	Group 0	Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII		Group VIII		
	Inert gases	E_2O EH		EO EH_2		E_2O_3		EO_2 EH_4		E_2O_5 EH_3		EO_3 EH_2		E_2O_7 EH				
		A	B	A	B	A	B	A	B	A	B	A	B	A	B			
1		1 H 1.008																
2	2 He 4.003	3 Li 6.94		4 Be 9.02		5 B 10.82		6 C 12.01		7 N 14.008		8 O 16		9 F 19				
3	10 Ne 20.183	11 Na 22.97		12 Mg 24.32		13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.06		17 Cl 35.45				
4	18 A 39.94	19 K 39.09		20 Ca 40.08		21 Sc 45.10		22 Ti 47.9		23 V 50.95		24 Cr 52.01		25 Mn 54.93		26 Fe 55.85	27 Co 58.94	28 Ni 58.69
			29 Cu 63.57		30 Zn 65.38		31 Ga 69.72		32 Ge 72.60		33 As 74.91		34 Se 78.96		35 Br 79.91			
5	36 Kr 83.7	37 Rb 85.48		38 Sr 87.63		39 Y 88.92		40 Zr 91.22		41 Cb 92.91		42 Mo 95.95		43 Tc —		44 Ru 101.7	45 Rh 102.9	46 Pd 106.7
			47 Ag 107.88		48 Cd 112.41		49 In 114.76		50 Sn 118.7		51 Sb 121.76		52 Te 127.6		53 I 126.9			
6	54 Xe 131.3	55 Cs 132.91		56 Ba 137.36		57 to 71 Rare earths		72 Hf 178.6		73 Ta 180.88		74 W 183.92		75 Re 186.31		76 Os 190.2	77 Ir 193.1	78 Pt 195.2
		—	79 Au 197.2		80 Hg 200.6		81 Tl 204.3		82 Pb 207.2		83 Bi 209.0		84 Po 210		85 At —			
7	86 Rn 222	87 Fr —		88 Ra 226.0		89 Ac 227		90 Th 232.1		91 Pa 231		92 U 238.07		93 Np —		94 Pu —	95 Am —	96 Cm —

like manner, each element in Series 3 resembles the element just above it in the same group.

This striking recurrence in properties with every eighth element was first observed by Newlands and is known as the *law of octaves* (meaning "eight") which reminds one of the octaves on a musical instrument. Beginning with the Series 4, this recurring relationship shifts from 8 to 18 and thus we have the long series arrangement. For example, in Series 4, we pass from argon to nickel, then (in Series 4) from copper to bromine and, finally, back to the inert gas krypton (through 18 elements).

3. The Periodic Law. This striking recurrence of similar properties every eighth or eighteenth element is expressed in the periodic law which states that the *properties of the elements are periodic functions of their atomic weights* (*or atomic numbers*). This law may perhaps be better understood if we refer to the musical scale. Starting at middle C on a piano, we have the keys designated, D, E, F, G, A, B, C, the latter C being one octave above middle C. Just as the pitch of a key is related to its position in the scale, the properties of an element are related to its position in a series of elements arranged in order of their atomic weights.

4. General Statement. We conclude from the study of the periodic table that (1) elements with similar properties are arranged in vertical groups known as families. With increasing atomic weight in a given family, the metallic character of the elements becomes more pronounced. There are also subgroups within the groups. (2) If the elements are arranged horizontally in order of their increasing atomic weights, every eighth or eighteenth element (depending upon the series) has similar properties. There are a few exceptions to this principle; for example, there are slight irregularities in the two pairs of elements argon and potassium; tellurium and iodine. These irregularities are corrected in the Moseley atomic number system (see Tables II and III).

5. Use of the Periodic Table. The periodic table has been of great value in guiding research both in theoretical and in applied chemistry. For example, Midgley found it very useful in his research on Freon, CF_2Cl_2, the widely used refrigerant. Another interesting illustration may be mentioned. The first electric-light bulbs made by Edison contained carbon filaments. More efficient filaments were made from the metal osmium, which is very rare and expensive. A study of the periodic table indicated that the neighboring elements, tantalum and tungsten, might be used in the place of osmium. Tungsten was less expensive than osmium, but special methods had to be developed for making tungsten filaments. The tungsten filament was found to be much more efficient than osmium.

6. Number of Elements Known. According to the original Moseley atomic number system, there were places for 92 elements with hydrogen, atomic No. 1, as the first and lightest element and with uranium, atomic No. 92, as the last and heaviest element in the list. At present, 95 elements have been recognized and assigned to positions as indicated in Table III in the modern periodic system.[1] There are, however, several elements the discovery of which has been announced within recent years and which have been given new names. Two of these elements are listed in Group VII: No. 43, technetium, Tc, meaning "artificial" (old name masurium); No. 85, astatine, At, meaning "unstable" (old name alabamine). The third element, No. 87, francium, Fr, from France (old name virginium), is listed in Group I. As a result of the extensive research on the development of the atomic bomb, two elements: No. 93, neptunium, Np, and No. 94, plutonium, Pu, have been identified. These latter elements are made from the element uranium. Two other elements: No. 95, Americium, Am, and No. 96, Curium, Cm, which are formed by nuclear transformation, have also been added to the list.

It is interesting to note that, many years ago, chemists had predicted the discovery of the elements ekaiodine, now called astatine, and ekacesium, now called francium. The prefix eka- means "beyond."

Exercises

1. From your knowledge of the halogen family of elements, predict some of the properties of ekaiodine or astatine, No. 85. From your knowledge of the metals, sodium and potassium, predict some of the properties of ekacesium or francium, No. 87.

2. The elements, selenium, Se, and tellurium, Te, resemble sulfur (Group VI). In the following table, write (*a*) the formulas of the compounds of selenium and tellurium corresponding to the formulas of the sulfur compounds, (*b*) the names of all these compounds under the respective formulas.

Sulfur compounds	Selenium compounds	Tellurium compounds
H_2S		
H_2SO_3		
H_2SO_4		

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[1] Foster, *J. Chem. Education*, 23, 603 (1946). (With additions.)

TABLE III

PERIODIC CLASSIFICATION OF THE ELEMENTS (MODERN PLAN)

(Atomic numbers are placed above the symbols of the elements; atomic weights below the symbols)

Group	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0	
Type	R_2O RH	RO RH_2	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4			R_2O	RO	R_2O_3	RO_2 H_4R	R_2O_5 H_3R	RO_3 H_2R	R_2O_7 HR	Inert gases	
Period 1 2 elements	1 H 1.0080																	2 He 4.003	2
Period 2 8 elements	3 Li 6.940	4 Be 9.02											5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.0000	9 F 19.00	10 Ne 20.183	2 8
Period 3 8 elements	11 Na 22.997	12 Mg 24.32	Transitional Elements										13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944	2 8 8
Period 4 18 elements	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7	2 8 18 8
Period 5 18 elements	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3	2 8 18 18 8
Period 6 32 elements	55 Cs 132.91	56 Ba 137.36	57 *58–71 La 138.92	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po (210)	85 At	86 Rn (222)	2 8 18 32 18 8
Period 7	87 Fr	88 Ra 226.05	89 **90–96 Ac (227)																

*Rare earth elements (Lanthanide series) Group IIIa	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61	62 Sa 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.94	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

**Actinide series Group IIIa	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np (238)	94 Pu (238)	95 Am (242)	96 Cm (243)

Courtesy of Journal of Chemical Education.

3. The elements, molybdenum, Mo, and tungsten, W, are also found in Group VI. Write (*a*) the formulas for molybdic and tungstic acids (analogous to sulfuric acid), (*b*) the formulas and the names of the ammonium salts of these acids.

7. Atomic Structure. The explanation for the above regularity in the properties of the elements lies in the structure of the atoms of the elements, which has already been discussed (IX. 2).

8. Isotopes. Nuclear Structure and Transmutations. Shortly after the discovery of radioactivity, it was found that ordinary lead had a different atomic weight than the lead that is formed in radioactive decomposition. There are actually several different forms of lead (isotopes of lead) which are all chemically alike except in atomic weights. *Isotopes are elements whose atoms are alike except as to atomic weight.* Their nuclei contain the same number of protons but different numbers of neutrons. The term *isotope* means "the same place" (in the periodic system). The simplest isotopes are those of hydrogen, of which there are three. Protium has atomic number 1 and atomic weight 1, ${}_1H^1$; deuterium has atomic number 1 and atomic weight 2, ${}_1H^2$; tritium has atomic number 1 and atomic weight 3, ${}_1H^3$. The weight or mass of an atom is concentrated at its nucleus so the atomic structure diagrams for these isotopes could be indicated as shown in Fig. 1. Ordinary hydrogen is a mixture of about 5,000 parts of protium with 1 part of deuterium, while tritium is present in this mixture in a much smaller proportion than deuterium. The properties of the various isotopes of a given element are almost identical. Their separation is a very difficult process. An apparatus known as the *mass spectrograph* has been used by F. W. Aston and others in the study of isotopes.

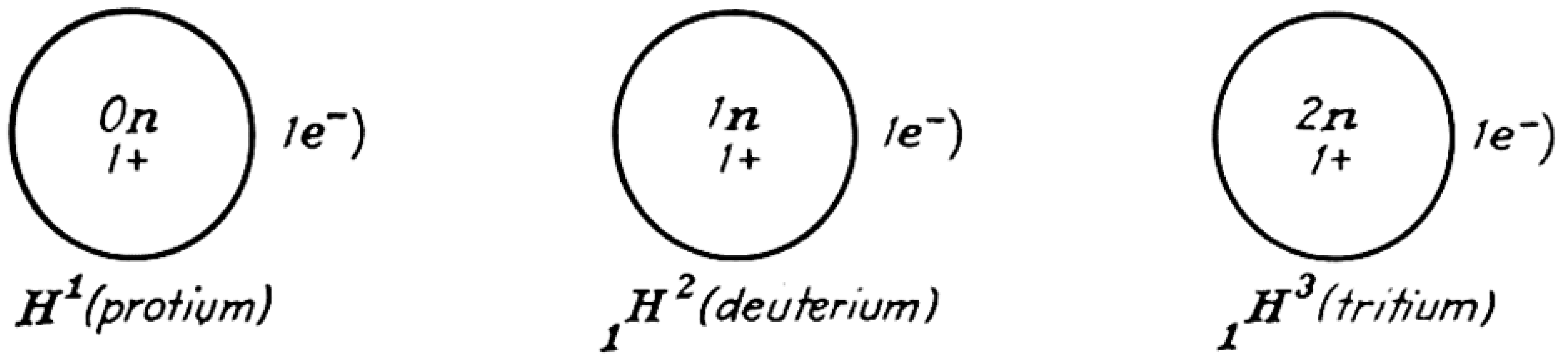

FIG. 1. Structures of the isotopes of hydrogen.

There are two isotopes of chlorine whose atoms have the structures shown in Fig. 2. Ordinary chlorine is a mixture of about three parts ${}_{17}Cl^{35}$ and one part ${}_{17}Cl^{37}$ giving an average atomic weight of about 35.46. Most other fractional atomic weights can be explained in the same way.

An important use of isotopic atoms promises to be as tracers in studying complicated processes such as digestion, plant growth, and catalysis. Thus the passage of water through a plant can be traced if some heavy hydrogen is present in the water absorbed. The water just absorbed can be distinguished from that present before absorption started. In a similar way, the digestion of foods and the course of drugs in the body can be traced if these foods or drugs contain even a slight concentration of heavy hydrogen, heavy oxygen, heavy nitrogen, or heavy carbon. Radioactive isotopes of sodium and phosphorus are also useful as tracer elements. Their course may be followed by detecting their radioactivity.

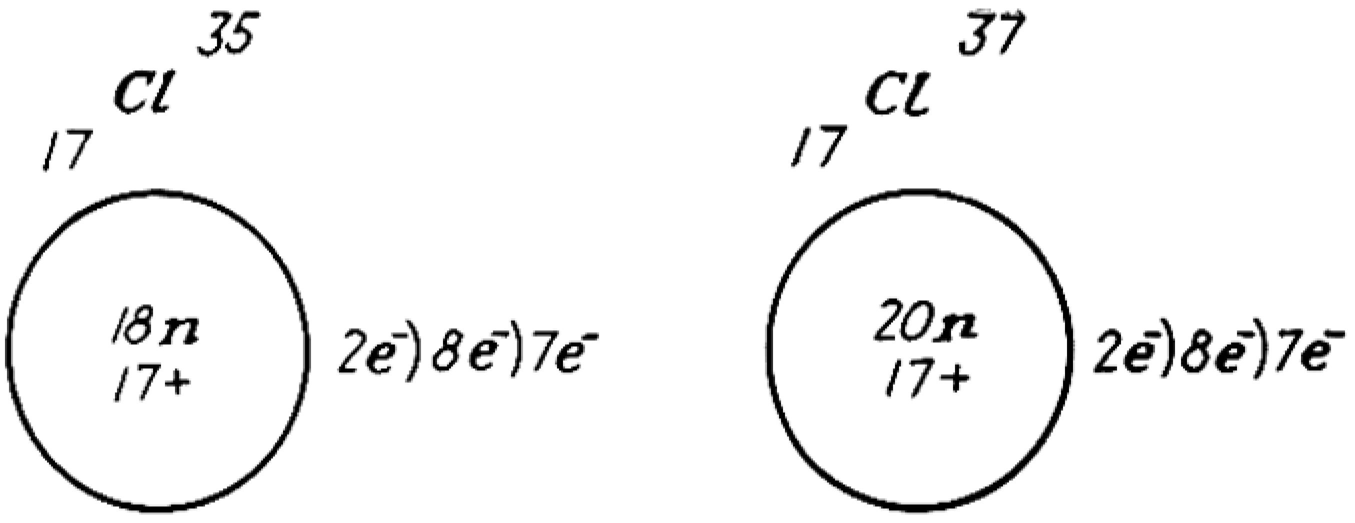

FIG. 2. Structures of the isotopes of chlorine.

The explanation for the existence of isotopes lies in the make-up or structure of the nuclei of atoms. This has been a most active field of research during the past few years.

The nucleus of an atom is formed by the union of protons and electrons in some fashion not yet completely understood. A proton is a particle of mass 1 and charge 1^+, being identical with the nucleus of ordinary hydrogen (protium). A proton and an electron can, apparently, fuse together under certain circumstances to form a neutron having mass 1 and no charge. The nucleus of a deuterium atom is composed of a neutron and a proton thus giving rise to mass 2 with charge 1^+ (a deuteron). Two neutrons and two protons combined produce an *alpha particle* of mass 4 and charge 2^+ identical with the nucleus of the helium atom. Three alpha particles combined produce the nucleus of an ordinary carbon atom having mass 12 and charge 6^+. However, if three alpha particles combine with a neutron, the nucleus of an isotope of carbon (mass 13, charge 6^+) is formed. It is to be noted that it is the charge on the nucleus and not the mass that characterizes the element. A given element may have atoms of several different weights, and it is thus evident that isotopic forms arise. The table of stable isotopes, (Seaborg, 1944) lists over 50 isotopic elements, among which are bromine, copper, mercury, silver, tin, etc. A number of isotopes with radioactive properties have been found in the products from nuclear disintegration.

Fundamentally, the nuclei of different atoms differ because they may be considered to be made up of different numbers of protons and electrons that have united to form neutrons and alpha particles. These in turn unite to form nuclei as described above for helium and for carbon.

Exercises

4. Indicate the number of protons and neutrons required for the nuclei of each of the following atoms:

$$_1H^1,\ _1H^2,\ _1H^3,\ _2He^4,\ _6C^{12},\ _6C^{13},\ _7N^{14},\ _7N^{15},\ _8O^{16},\ _8O^{18}$$

5. Indicate how the protons and neutrons would be united to form alpha particles and neutrons within the nuclei of each of the following atoms:

$$_2He^4\ _6C^{12},\ _6C^{13},\ _8O^{16},\ _8O^{18}$$

Much of the information concerning the nucleus has been obtained from experiments in which atoms of an element are bombarded by rapidly moving protons, alpha particles, neutrons, or deuterons. Because the nucleus of an atom is positively charged and because protons, alpha particles, and deuterons are also positively charged, these latter bombarding particles must be given enormous velocities and energies to overcome the repulsion between the two positively charged particles and strike the nucleus with enough energy to cause any change to occur. The situation is made more difficult because, even though the nucleus of an atom has practically all the mass of an atom, it occupies only a very small part of the volume of the atom. Thus many bombarding particles miss the nucleus entirely, many others are repelled or deflected due to insufficient speed, and only a small proportion actually strike the nucleus as desired. The original source of bombarding particles was radium or some other radioactive element. The disintegration of radium involves the formation of alpha particles traveling at very high speeds. Subsequently, methods were devised for producing neutrons by the cyclotron and the atomic pile. The neutron, lacking a charge, can approach nuclei at a slower speed. By such means it has been possible to achieve the transmutation of elements.

Transmutation processes involve not only the change of one kind of atom into others, but also the liberation of energy in amounts quite large compared with the weights involved. This energy arises from the conversion of a part of the mass of the original atoms into energy so that there is a loss in weight during the change. At present, such transmutation processes are very inefficient and very costly. No

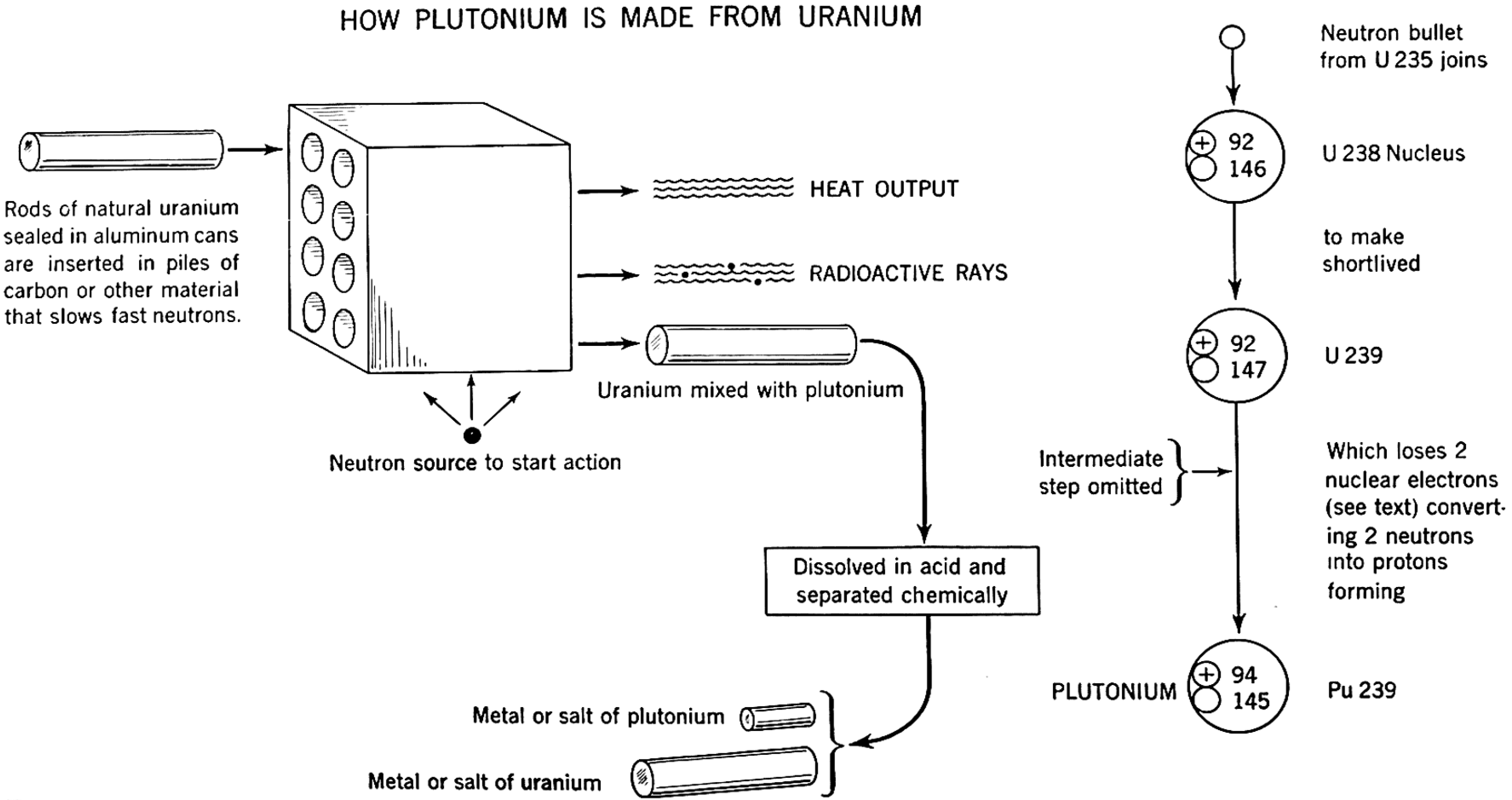
HOW PLUTONIUM IS MADE FROM URANIUM
Rods of natural uranium sealed in aluminum cans are inserted in piles of carbon or other material that slows fast neutrons.
HEAT OUTPUT
RADIOACTIVE RAYS
Uranium mixed with plutonium
Neutron source to start action
Dissolved in acid and separated chemically
Metal or salt of plutonium
Metal or salt of uranium
Neutron bullet from U 235 joins
92
146
U 238 Nucleus
to make shortlived
92
147
U 239
Intermediate step omitted
Which loses 2 nuclear electrons (see text) converting 2 neutrons into protons forming
PLUTONIUM
94
145
Pu 239

FIG. 3. Man-made plutonium—U235 substitute. (*From Weaver and Foster, "Chemistry for Our Times," McGraw-Hill Book Company, Inc.*)

practical progress has been made toward the large-scale production of useful expensive elements, *e.g.*, helium, or toward the practical use of nuclear energy, except in the case of the atomic bomb.

9. The Atomic Bomb. The tremendous amount of atomic energy released in the explosions of the atomic bombs—the first experimentally, in New Mexico, the second and third at Hiroshima and Nagasaki in Japan (summer of 1945) and others subsequently at Bikini—is far greater than the amount of energy per unit weight released from any other explosive.

The development of the atomic bomb was based upon (1) the production of the element *plutonium*, ${}_{94}Pu^{239}$, from uranium, U, by bombardment of uranium with neutrons under controlled conditions, (2) the separation of the *uranium isotope*, ${}_{92}U^{235}$ (0.7 per cent) from the more abundant common isotope, ${}_{92}U^{238}$ (99.3 per cent). Both plutonium and the U235 isotope are less stable than the more abundant ${}_{92}U^{238}$ isotope.

In a given period of time, an appreciable fraction of the atoms in a sample of plutonium, Pu, or U235 undergo radioactive decomposition producing neutrons. These neutrons cause additional atoms to disintegrate. This process, in turn, produces more neutrons which cause still more atoms of plutonium or U235 to disintegrate. The process becomes a *chain reaction*, which proceeds with increasing rate. The reaction is controlled by interposing bars of cadmium or other material which absorbs a certain proportion of the neutrons without further action. An alternative procedure is to limit the size of the samples of plutonium or U235 so that the majority of the neutrons escape into the surrounding medium. Samples of plutonium or U235 that are larger than a definite critical mass undergo the uncontrolled chain reaction characteristic of the atomic bomb detonation. The controlled action of disintegrating uranium, plutonium, Pu, and other elements is of great scientific value and interest in developing (1) isotopes for tracer studies (Sec. 8) and (2) atomic power plants.

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CHAPTER XVII

THE ATMOSPHERE

In the study of oxygen, we have learned that air is a mixture of gases commonly known as the *atmosphere*. In this chapter, we are to consider some of its properties and its role in life and industry. The inert gases found in the atmosphere will also be considered.

1. Composition. Air is remarkably constant in composition, owing to constant mixing by the winds. Ordinarily, air is considered to be one-fifth oxygen and four-fifths nitrogen by volume. This is only an approximation. The actual composition is very close to 21 per cent oxygen, 78 per cent nitrogen, and 1 per cent argon. In addition, the other rare gases, neon, krypton, xenon, and helium are present in minute but quite constant amounts. Dust, carbon dioxide, and water vapor are important components of air, but these are present in variable amounts.

Important contributions to our knowledge concerning the upper atmosphere, or stratosphere, have been made as a result of balloon flights in 1934 and 1935 sponsored by the U. S. Army Air Corps and The National Geographic Society.[1] On Nov. 11, 1935, the balloon, Explorer II, ascended to a height of 13.7 miles. A vast amount of scientific data relating to meteorology, biology, and physics was collected. For example, the atmospheric pressure at 13.7 miles was about 30 mm. which is only $^{30}/_{760}$ or 4 per cent of the pressure at sea level. This means that 96 per cent of the atmosphere is below the 13.7-mile level. Very low temperatures (−78°F.) were recorded. The sunlight was very intense, probably owing to the absence of dust. The sky, however, appeared blue-black in color. Samples of air collected during the flight and analyzed later at the U. S. Bureau of Standards contained the same proportions of oxygen and other components as the air at the ground level. To sustain life within the sealed gondola, a liquid oxygen-nitrogen mixture was provided. The exhaled air was purified by passing it through a vessel containing sodium hydroxide which absorbed carbon dioxide and water vapor. About 3,700,000 cu. ft. of the inert, noncombustible gas, helium, was used to inflate the balloon. The information obtained by these investigations of the stratosphere is doubtless of great value in high-altitude flying both in war and in commerce. The names of Major Anderson and Captain Stevens, who conducted these flights, rank high in the list of explorer-scientists along with William Beebe and Richard Byrd, who have pushed back the frontiers of our knowledge of the air, the ocean, and the polar regions.

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[1] *The National Geographic Magazine*, October, 1934; January, 1936.

2. Humidity. The actual percentage of water vapor in air is not so important as the *relative humidity* or percentage of humidity. This may be defined as the ratio of the actual moisture content to the maximum moisture content. For purposes of calculation:

$$\%\text{ humidity} = \frac{\text{actual pressure of water vapor in air}}{\text{maximum pressure of water vapor in air}} \times 100$$

The maximum pressure of water vapor is the vapor pressure of water (aqueous tension) that corresponds to the temperature of the air. The actual pressure may be obtained if the total air pressure (barometric pressure) and the percentage by volume of moisture in the air are known.

$$\text{Actual pressure} = \text{barometric pressure} \times \frac{\%\text{ moisture}}{100}$$

Example. A sample of air analyzes 0.75 per cent water vapor. The barometric pressure is 725 mm. and the temperature 22°C. Calculate the percentage of humidity.

Answer: $\dfrac{725 \times \dfrac{0.75}{100}}{19.7} \times 100 = 27.6\%$ humidity

Exercise

1. Using the above method of calculation, fill in the blanks in the following table:

% moisture in air	Barometric pressure	Temperature	Maximum pressure	Actual pressure	% humidity
0.2	765	10°C.			
0.5	748	30°C.			
0.93	733	26°C.			
1.1	720	15°C.			

3. Humidity and Comfort. The temperature of the body is controlled largely by the evaporation of water through the skin.

More rapid evaporation produces a greater cooling effect. The rate of evaporation is controlled largely by the humidity of the air. A low humidity causes relatively rapid evaporation and therefore causes a feeling of coolness. When humidity is high, an additional cooling effect is secured by circulation of air so as to displace air of highest humidity immediately next to the skin.

4. Air Conditioning. Four factors are involved in the conditioning of air to make it suitable for living rooms, public buildings, and manufacturing plants: (1) control of temperature, (2) control of humidity, (3) purification, (4) circulation.

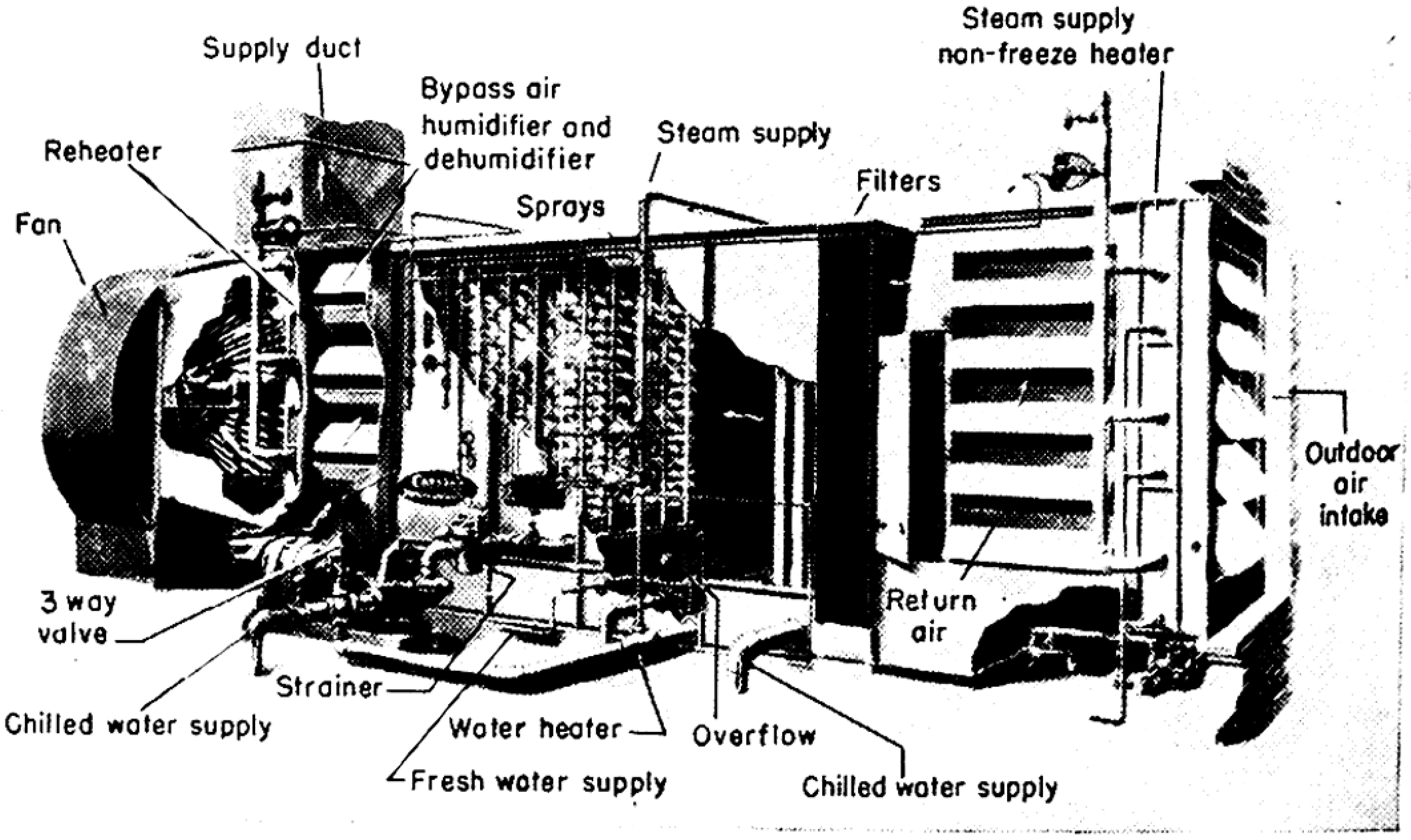

FIG. 1. Air-conditioning system. (*Carrier Corporation.*)

The air in living rooms, for example, is regarded as comfortable if the temperature is 68 to 70°F., and the relative humidity is about 40 per cent. The air should be free from dust and circulated by fan or otherwise. Air in houses heated by hot water or steam usually has a low relative humidity which may be increased by use of tanks or pans containing water, which may be attached to the radiators. Newer types of warm air heating equipment control all four factors in air conditioning and are practically automatic in operation.

5. Proof That Air Is a Mixture. The relatively constant composition of air might mistakenly be taken as proof that it is a compound. The best proof that air is a mixture is its behavior upon partial liquefaction, whereupon the liquid is found to be mainly oxygen. Obviously, a compound would have the same proportion of oxygen after liquefaction as before. Equally sound proofs are based upon the behavior of liquid air during partial evaporation and upon the solubility of air in water. In the latter case, the proportion of oxygen is much greater in the dissolved air.

6. Liquefaction of Air. This depends upon the application of the important principle that a compressed gas absorbs heat upon expansion. Obviously, if a gas is compressed, the opposite heat change (liberation of heat) will occur and the gas will become warm or hot. The more important units in a liquid-air machine are indicated in Fig. 2.

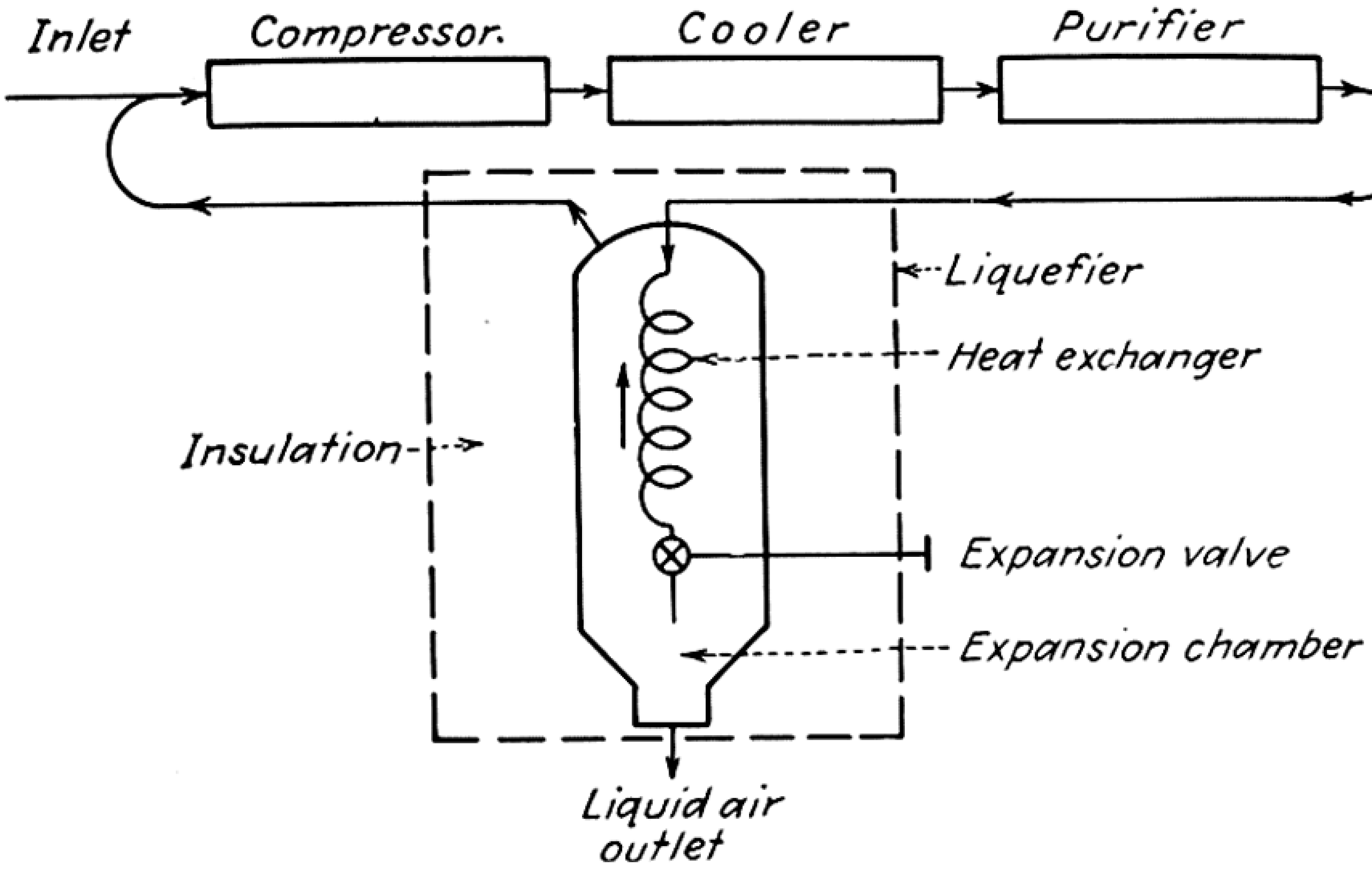

FIG. 2. Liquid-air machine (flow diagram).

The compressor unit compresses the air to about 3,000 lb. per sq. in. whereupon the air becomes very hot. It is cooled to room temperature by passing through a tank of cold water. The purifier contains calcium chloride, $CaCl_2$, or potassium hydroxide, KOH, or similar materials that remove moisture and carbon dioxide from the air. At the low temperature of the liquid air, these compounds would become solid and block the air passages.

The liquid air is actually produced in the liquefier which is very well insulated since temperatures of -190°C. must be reached inside the expansion chamber where the liquid air is formed. Even under the best of conditions only a portion of the air is liquefied. The cold but unliquefied air is returned to the compressor by way of the heat exchanger. At the heat exchanger, the cold air returning to the compressor comes in close contact with the tube containing the relatively warm air that is just entering the liquefier. As a result, the incoming warm air is greatly precooled even before it reaches the expansion valve. In passing through the latter, the pressure of the air drops from about 200 to 1 atm., and the resulting expansion lowers the temperature of the air so much that some of it liquefies. Obviously, better precooling in the heat exchanger results in a larger proportion of air liquefaction. The design of the heat exchanger is, therefore, an important matter.

Exercise

2. Reproduce the diagram of a liquid-air machine and explain the exact function of each part.

7. Liquid-air Products. Liquid air is the industrial source of nitrogen, oxygen, argon, neon, krypton, and xenon. The last four gases named constitute only about 1 per cent of air. The fact that these gases in the liquid state have different boiling points makes it possible to separate them by the fractional distillation or fractionation of liquid air. For example, liquid nitrogen boils at −195.8°C., and liquid oxygen boils at −182.5°C.

Exercise

3. Which gas, oxygen or nitrogen, is present in greater quantity in the first portions distilled from liquid air?

Oxygen from liquid air is used extensively with acetylene for the cutting and welding of metals. Large quantities of nitrogen are used, with hydrogen, in the manufacture of ammonia.

8. Inert or Rare Gases of the Atmosphere. These elements are all characterized by their chemical inactivity. They form no compounds with other elements and so may be said to have only a zero valence. The external electron arrangements of their atoms may be summarized as shown in Table I. (Refer to Chap. IX.)

TABLE I

Symbol	Name	Atomic No.	External electron arrangement by levels
He	Helium	2	2
Ne	Neon	10	2, 8
A	Argon	18	2, 8, 8
Kr	Krypton	36	2, 8, 18, 8
Xe	Xenon	54	2, 8, 18, 18, 8
Rn*	Radon	86	2, 8, 18, 32, 18, 8

* Emanation from radium.

The inert gases (except helium) were discovered by the English chemists, Ramsay and Rayleigh, about 1895, during their investigations of nitrogen. The discovery of these elements resulted from experiments that these scientists made on the density of nitrogen prepared from air and from ammonium nitrite. The nitrogen prepared from the air had a slightly greater density than the nitrogen that they prepared from ammonium nitrite. Careful investigation revealed that this difference in density was due to the presence of the inert gases in the atmospheric nitrogen.

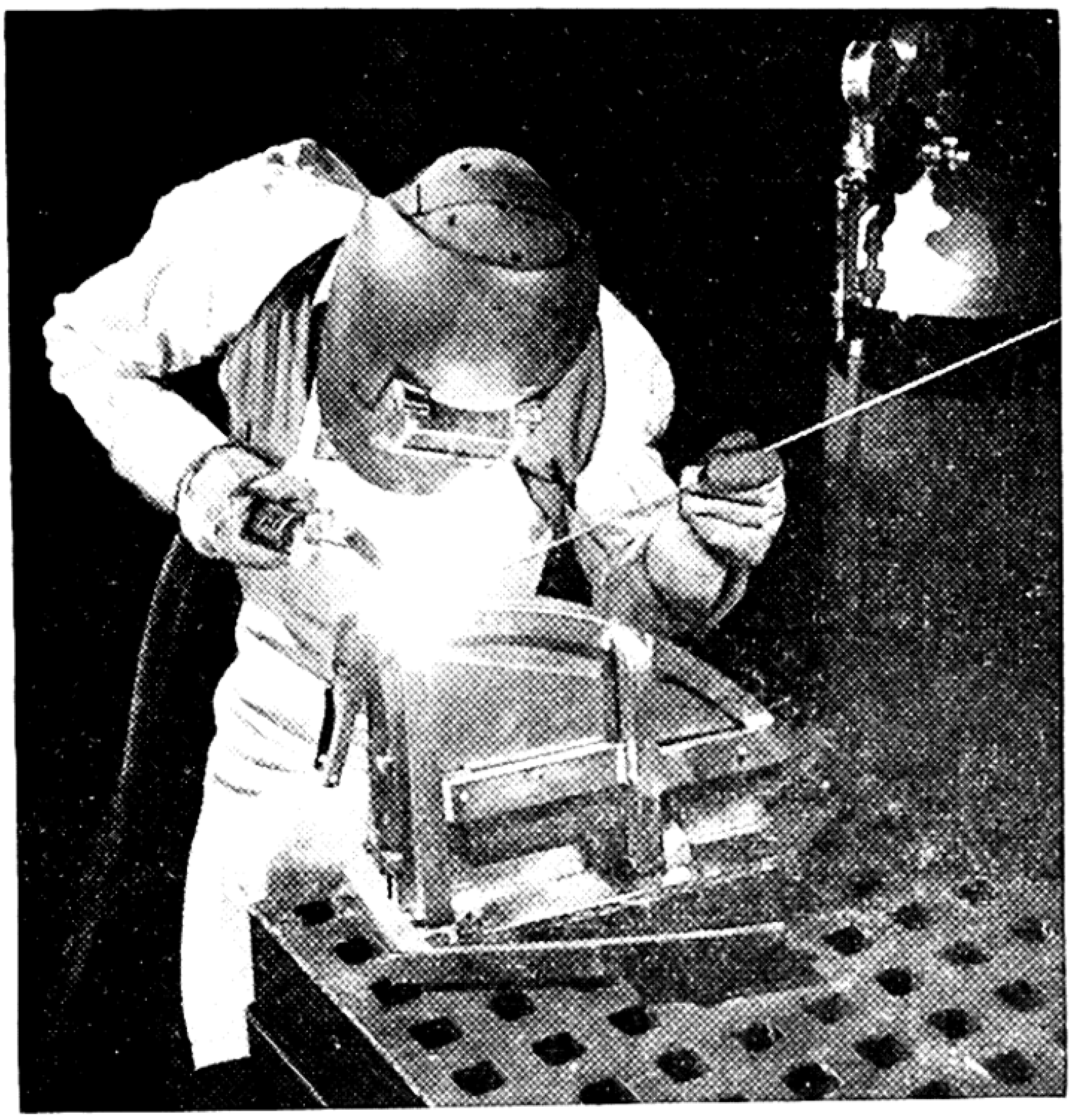

FIG. 3. Helium arc welding of magnesium. (*Dow Chemical Co.*)

Helium was discovered simultaneously by Janssen and by Frankland and Lockyer (1868) in the chromosphere of the sun. The name, helium, is a Greek word meaning "sun." Helium replaced hydrogen in the inflation of balloons and dirigibles, because of the fact that it does not burn. A plant for extracting helium from natural gas in Texas is owned and operated by the U. S. Government.

Helium mixed with oxygen under pressure is supplied in place of air to workmen engaged in the excavation of tunnels under rivers. Since helium is less soluble in the blood than nitrogen, the possibility of the dread effects known as the *bends* is greatly reduced. Since helium does not support combustion, it is used in welding magnesium (XXVIII. 18).

Neon, when placed in glass tubes under reduced pressure and a suitable electrical potential, presents the familiar bright-red color effect observed in electric signs.

Argon is used in electric-light bulbs in order to decrease the rate of evaporation of the hot metal filament. The inert property of argon prevents the formation of a compound of this element with the tungsten in the filament.

Exercise

4. Which of the rare gases occurs in appreciable amounts elsewhere than in air?
5. Which of the rare gases was discovered in the sun before it was found on the earth?
6. Which of the rare gases occur in connection with radioactive minerals?
7. What is the chief commercial source of (*a*) helium, (*b*) neon, (*c*) argon, (*d*) radon?
8. State the two chief uses of helium.
9. State one use of (*a*) neon, (*b*) argon, (*c*) radon.
10. What is the number of valence electrons in the inert gases?

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CHAPTER XVIII

NITROGEN AND AMMONIA

The element nitrogen, N_2, and the compound ammonia, NH_3, are essential materials in the manufacture of fertilizers and explosives and in industrial refrigeration systems. In the study of the manufacture of synthetic ammonia and its use in refrigeration, we shall consider two very interesting scientific principles.

1. Nitrogen. The atmosphere, as already stated, contains 78 per cent nitrogen and 21 per cent oxygen. Since air is colorless and less reactive than oxygen, it follows that nitrogen must be a colorless and a relatively inactive gas. Animals placed in a chamber containing nitrogen soon die from suffocation.

Since nitrogen, in compound form, is involved in the growth of plants and animals, it is an essential element in fertilizers and foods. The excreta of animals contain combined nitrogen which is readily available to plants when applied to the soil. Animal manures are usually supplemented by prepared fertilizers containing sodium nitrate, $NaNO_3$, ammonium sulphate, $(NH_4)_2SO_4$, and other compounds. A more detailed consideration of fertilizers is presented in Chap. XX and in courses in agronomy.

Exercises

1. Calculate the relative density of O_2 and N_2 using the gram molar volume principle.

2. Explain why the heavier O_2 does not settle to the earth and thus change the percentage composition of the air at the surface of the earth.

2. Chemical Properties of Nitrogen. In contrast to oxygen, nitrogen is relatively inactive although it does react with certain other elements and compounds under the proper conditions. For example, it combines with hot magnesium, aluminum, and a few other elements, forming *nitrides*.

$$3Mg + N_2 \rightarrow Mg_3N_2$$

Carbon, sulfur, and other combustible substances, when first ignited in air and then placed in nitrogen, cease to burn.

3. Fixation of Nitrogen. Any process for converting the nitrogen gas of the atmosphere into a useful nitrogen compound is called *nitrogen fixation.* This process is accomplished naturally by means of the bacteria on the roots of certain leguminous plants, as well as by lightning. Nitrogen fixation is accomplished commercially by the *Haber process* and by the *cyanamide process.* The latter involves the heating of calcium carbide with nitrogen in an electric furnace, causing the following reaction:

$$CaC_2 + N_2 \rightarrow \underset{\text{calcium cyanamide}}{CaCN_2} + C$$

Calcium cyanamide is a solid that reacts with hot water.

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + \underset{\text{ammonia}}{2NH_3}$$

Nitrogen fixation is most essential in order that the fertility of soils and therefore the yields of crops may be maintained. The uncombined nitrogen of the air is useless for plant growth, but nitrogen compounds are absolutely essential for proper growth. Nitrogen compounds are also essential in connection with warfare and with blasting and construction work.

Exercise

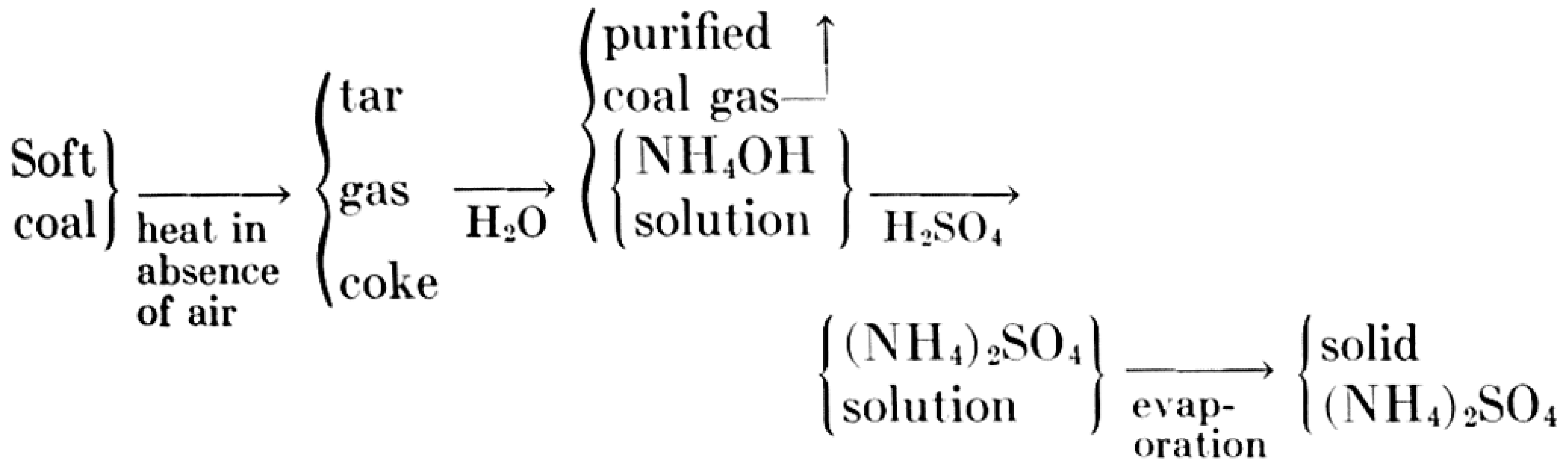
3. Calculate (*a*) the weight of calcium cyanamide formed by the reaction of 1,000 g. calcium carbide with an excess of nitrogen; (*b*) the volume of nitrogen at 400°C. and 750 mm. pressure required to react with 1,000 g. calcium carbide.

AMMONIA

4. Industrial Importance and Uses. Ammonia, NH_3, is used extensively in refrigeration because it is easily liquefied by pressure and because the liquid gives a large cooling effect when it vaporizes. It is also used in the manufacture of *sodium carbonate* (soda ash or washing soda). Large quantities of sodium carbonate are used in glass manufacture and in the softening of hard water. Ammonia is also used in the production of fertilizers, *e.g.*, ammonium sulfate and ammonium phosphate and the explosive, ammonium nitrate. Large amounts of ammonia are used in the manufacture of nitric acid, which is in turn converted to fertilizers, explosives, celluloid, and other plastics and resins, dyes, and drugs.

5. Manufacture of Ammonia. Ammonia is produced by the action of heat on soft coal in the absence of air. This is called *destruc-*

tive distillation of coal. The main products of this process are coke, coal tar, and coal gas. The coal gas is passed through water which dissolves the small proportion of ammonia present, while the remainder of the coal gas passes on unchanged. The ammonia solution (ammonium hydroxide) is neutralized by sulfuric acid and the ammonium sulfate is recovered by evaporation. The entire process may be described in outline form by a flow diagram as follows:



At the present time ammonia is manufactured largely by the direct union of the elements nitrogen and hydrogen.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}$$

This is called the *Haber process.*

6. Haber Process. In this process, purified hydrogen and nitrogen in correct proportions are passed over a catalyst at a temperature as high as 550°C. (nearly red heat) and a pressure as high as 1,000 atm. At 500°C. and 300 atm., about 25 per cent of the incoming gases combine to form ammonia. The ammonia is separated, and the uncombined hydrogen and nitrogen are passed through the process again. The catalyst may consist of a specially prepared mixture of iron and molybdenum with smaller amounts of other elements. The commercial catalysts consist of iron with potassium, sodium, or other elements. It is necessary to construct the apparatus of special alloy steels that will withstand the extremely high temperature and pressure. This process is of major importance in national and world affairs because of its relation to the production of fertilizers, explosives, plastics, dyes, and drugs.

The question naturally arises as to why only about 25 per cent of the nitrogen and hydrogen unite, and how this low yield may be increased. Higher temperatures result in a decrease in yield, while higher pressures give increased yield. As a result, operating pressures have been increased from 200 to 1,000 atm. in the past 20 years. This has been made possible by the development of stronger alloy steels.

Lower temperatures result in higher yields, but the rate of the reaction is halved for every 10-deg. drop in temperature. For this reason, temperatures cannot be decreased below their present values without slowing the process down so much that it becomes impracticable. In fact, the only reason why the process is practicable at all is that the catalysts used increase the normal rate of the reaction sufficiently to allow the 25 per cent yield of ammonia to be formed during the comparatively short time when the gases are in contact with the catalyst.

The reason for the limitation of the yield is the reversible nature of the reaction:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + \text{heat}$$

With the temperature and pressure mentioned above, it is impossible to have more than 25 per cent ammonia present because, when this concentration is reached, the ammonia decomposes as rapidly as it forms. In other words, the forward and reverse reactions in the above equation have reached a state of equilibrium. Use of a catalyst has no effect on the proportions of ammonia in this mixture. The sole function of the catalyst is to decrease the time required for the original mixture of hydrogen and nitrogen to change to the equilibrium mixture. Changes in temperature and pressure do change the proportions in an equilibrium mixture, and by making use of Le Châtelier's principle the general nature of these effects can be determined without doing any experiments.

7. Le Châtelier's Principle. This may be stated in its most general form as follows: *If a stress is placed upon an equilibrium mixture, the action that relieves the stress is favored.* A stress is a change in temperature, pressure, or concentration. Thus, if the temperature of an equilibrium mixture is increased, the action that cools the mixture is favored. If the temperature is decreased, the action that produces heat and thus warms the mixture is favored. For practical purposes, the principle may be summarized as follows:

a. Increase in temperature favors action that uses heat.

b. Increase in pressure favors action that reduces the volume of the mixture.

For example, when the temperature of the equilibrium mixture $N_2 + 3H_2 \rightleftarrows 2NH_3 + \text{heat}$, is increased, it is the reverse reaction (to the left) that is favored because that reaction uses heat (NH_3 is also used, N_2 and H_2 are produced by the reverse reaction). Again, if the pressure on the mixture

$$\underbrace{N_2 + 3H_2}_{\text{4 vol.}} \rightleftarrows \underset{\text{2 vol.}}{2NH_3}$$

is increased, the forward reaction (to the right) is favored because it occurs with *decrease* in volume (from 4 to 2 volumes).

Exercises

4. Indicate which reaction, to the right or left, is favored in the following cases:

(*a*) Increased temperature on $C_2H_4 + H_2 \rightleftarrows C_2H_6$ + heat.
(*b*) Decreased temperature on $N_2 + O_2 \rightleftarrows 2NO$ − heat.
(*c*) Increased temperature on $2NO_2$ + heat $\rightleftarrows 2NO + O_2$.
(*d*) Decreased temperature on $N_2O_4 \rightleftarrows 2NO_2$ − heat.
(*e*) Increased temperature on $2SO_2 + O_2 \rightleftarrows 2SO_3$ + heat.
(*f*) Decreased pressure on reaction of (*a*).
(*g*) Increased pressure on reaction of (*b*).
(*h*) Decreased pressure on reaction of (*c*).
(*i*) Increased pressure on reaction of (*d*).
(*j*) Decreased pressure on reaction of (*e*).

5. State the best conditions of temperature and pressure for a good yield (in forward direction) in each of the reactions of Exercise 4, assuming that all the reactions are rapid.

8. Refrigeration. All ordinary refrigeration processes depend upon the following principle. When a liquefied gas vaporizes, it absorbs heat (has a cooling effect on itself and its surroundings). This may be expressed by a diagram (Fig. 1).

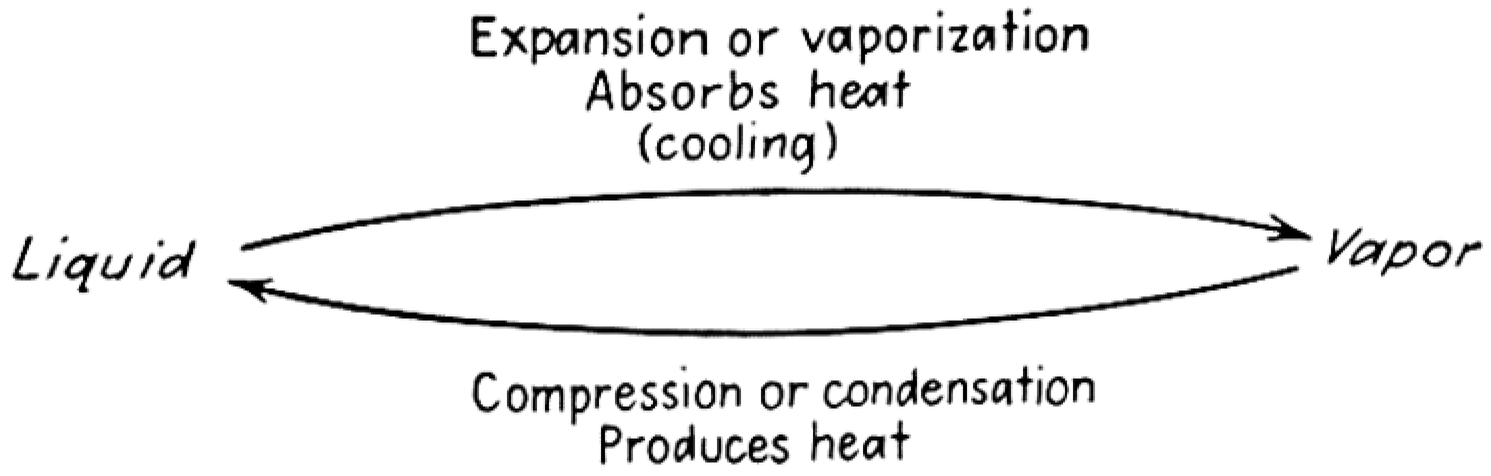


FIG. 1. Cooling by vaporization.

Figure 2 indicates the various parts and their arrangement in the most common type of refrigerating unit. The gas in the unit is warmed above room temperature by the compressor, but is then cooled to room temperature by the water or air cooler. This process usually results in liquefaction. Beyond the expansion valve, the liquid vaporizes and absorbs heat, and this effect is used to produce the desired refrigeration. Finally, the vapor is returned to the compressor.

The materials used in refrigeration units should be easily liquefied by pressure and should absorb much heat per unit of weight when the liquid changes to vapor. They should also be, as nearly as possible, nonpoisonous, noninflammable, nonexplosive, and have a characteristic odor. It is difficult to achieve all these characteristics in one substance. Some commonly used substances are ammonia, sulfur dioxide, methyl chloride, CH_3Cl, and dichlordifluoromethane, CCl_2F_2 (Freon). The latter compound is especially well adapted for use in household refrigerators. Other similar compounds are also used.

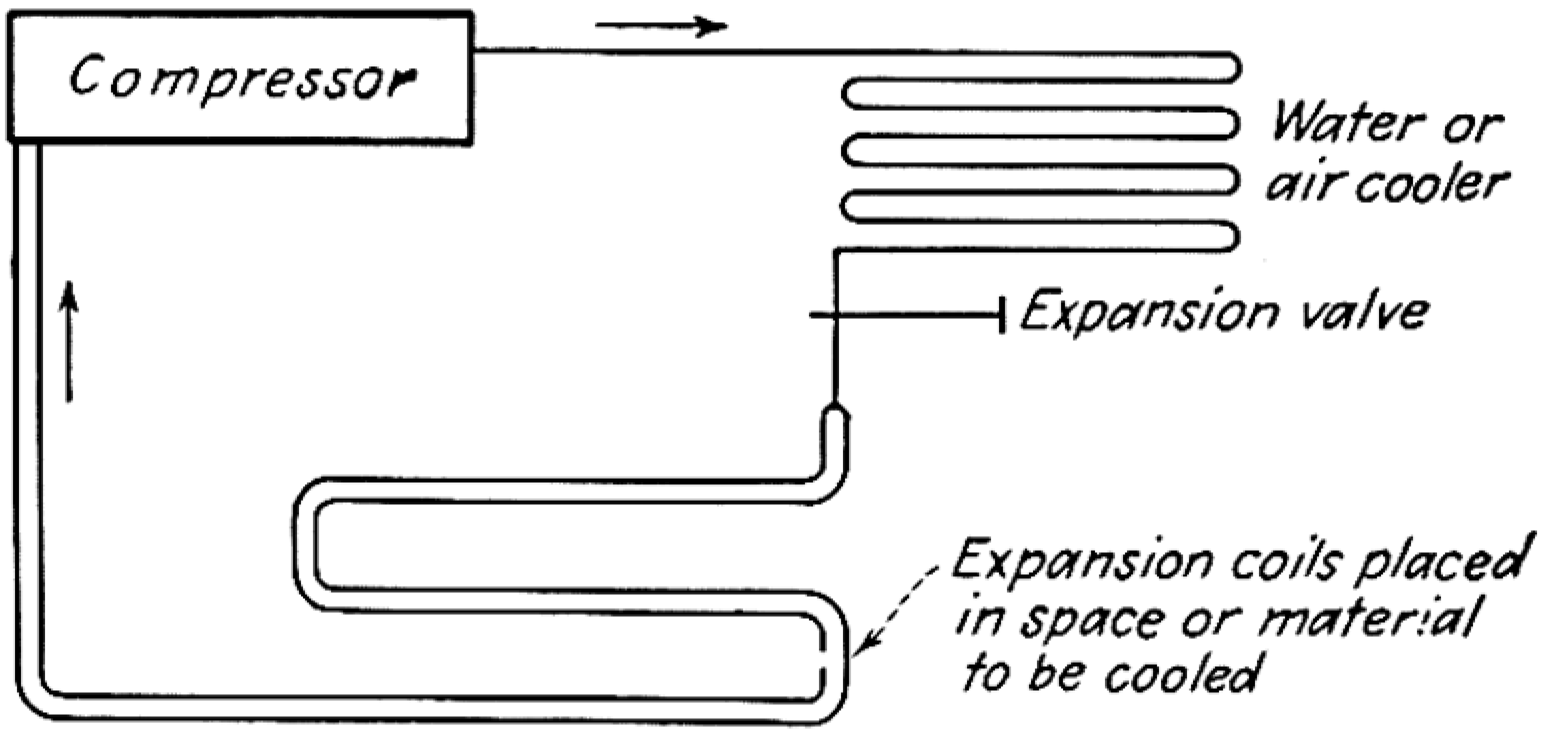


FIG. 2. Flow diagram of refrigeration.

The working parts of a household refrigerator are shown in Fig. 3. The process is essentially the same as that described and illustrated in Fig. 2. The reader should trace the cycle followed by the refrigerating gas, in the diagram of the household refrigerator.

9. Laboratory Preparation of Ammonia. This is most conveniently done by the reaction of lime with an ammonium salt with the application of some heat (see Sec. 13).

Exercise

6. Complete and balance the equations:

$$CaO + (NH_4)_2SO_4 \rightarrow NH_3 + H_2O + \text{———}$$
$$Ca(OH)_2 + NH_4Cl \rightarrow$$

10. Physical Properties of Ammonia. Ammonia is a colorless gas with a sharp odor, very soluble in water, and easily liquefied, even at ordinary room temperature under a pressure of approximately 8.5 atm. Liquid ammonia boils at −33.5°C. and, upon evaporation, absorbs 330 cal. heat per gram (heat of vaporization). For water, the heat of vaporization at 100°C. is 540 cal. per gram.

11. Chemical Properties of Ammonia. Ammonia unites with water to form ammonium hydroxide, a weak base.

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$$

It unites directly with acids to form ammonium salts.

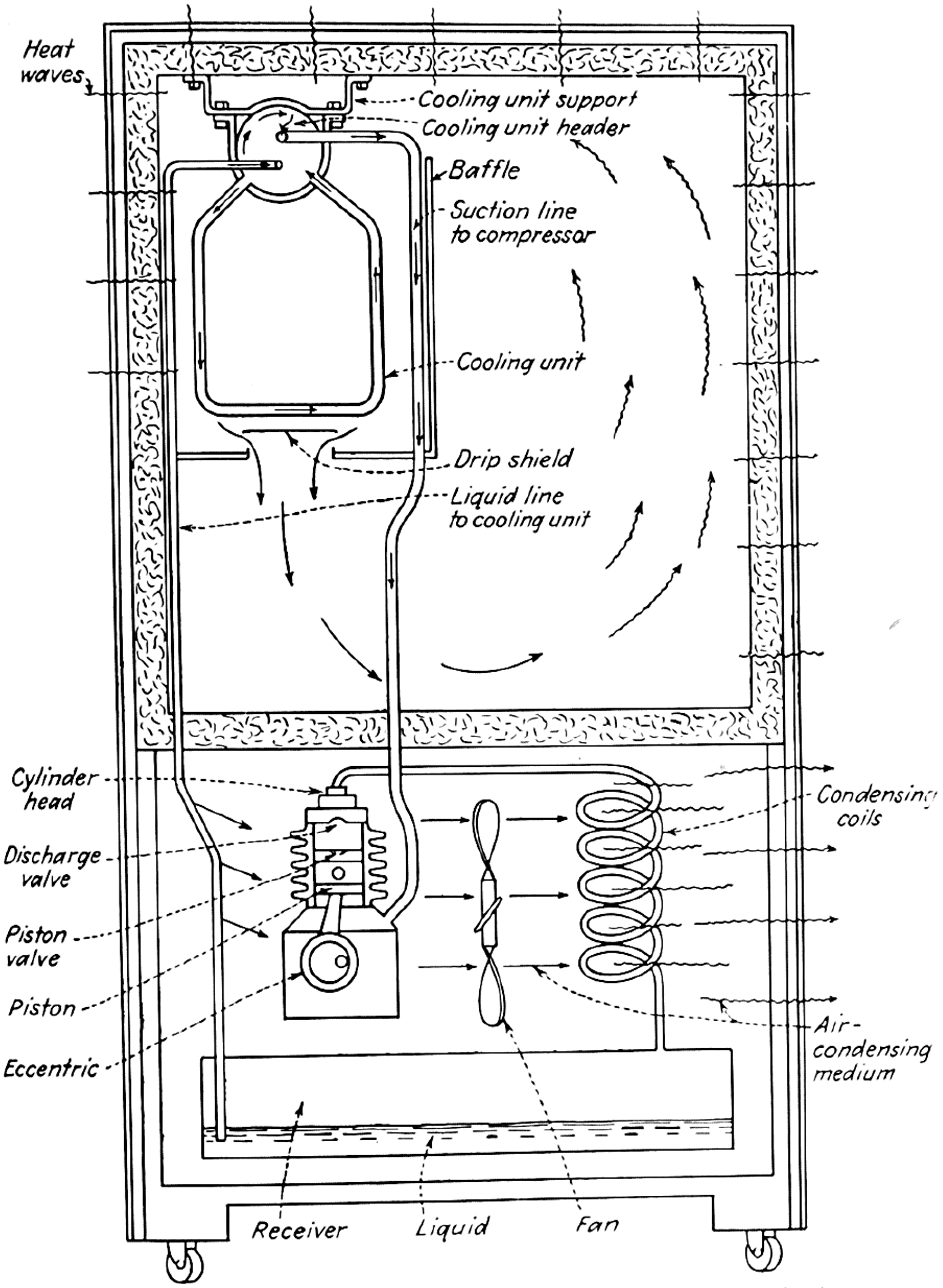


FIG. 3. Household refrigerator. (*General Motors Corporation.*)

12. Formation of Ammonium Salts. They may be formed by direct union of ammonia with an acid, or by neutralization of ammonium hydroxide by an acid.

Exercises

7. Write equations for the formation (by direct union) of (*a*) NH_4Cl, (*b*) NH_4NO_3, (*c*) $(NH_4)_2SO_4$, (*d*) $NH_4H_2PO_4$, (*e*) $(NH_4)_2CO_3$.
8. Write equations for the formation of the salts of Exercise 7 by neutralization.

13. Properties of Ammonium Salts. Ammonium salts are, in general, white solids quite soluble in water. They are decomposed by heat usually (but not always) into ammonia and an acid.

Ammonium salts dissociate into ions when dissolved in water, for example,

$$NH_4Cl \rightleftarrows NH_4^+ + Cl^-$$

All ammonium salts liberate ammonia when heated with a strong base, *e.g.*, NaOH or $Ca(OH)_2$. This is the basis for the laboratory preparation of ammonia, and also for the test for ammonium salts (or the ammonium ion). To test an unknown salt for ammonium ion, a sample of the salt is mixed with NaOH solution, or solid CaO or $Ca(OH)_2$, and the mixture is heated. Red litmus paper, held just above the mouth of the test tube, will turn blue.

Exercises

9. Write equations for the decomposition by heat of salts *a*, *c*, *d*, and *e*, of Exercise 7. Ammonia is formed in each of these cases.
10. Write equations for the ionization of five ammonium salts. What ion is present in all ammonium salt solutions?
11. Write five equations to illustrate the reaction taking place during the above test.

The liberation of ammonia is detected (*a*) by its odor, (*b*) by its action on moist red litmus paper, (*c*) by its blackening action on filter paper wet with mercurous nitrate solution. A slight blue color in the litmus test is not necessarily an indication of ammonia if NaOH solution is used in the test, because a fine spray of NaOH solution may reach the litmus paper in spite of considerable care to avoid this effect.

Exercise

12. Calculate the volume of ammonia gas formed at 100°C. and 750 mm. pressure, by heating 100 g. ammonium chloride with an excess of sodium hydroxide.

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CHAPTER XIX

NITRIC ACID AND EXPLOSIVES

Nitric acid, HNO_3, is a very important substance: in the laboratory as an oxidizing reagent, and in industry for the manufacture of explosives. To understand the chemistry of nitric acid, it will be helpful to turn our attention first to a brief study of the oxides of nitrogen.

1. Oxides of Nitrogen. *Nitrous oxide*, N_2O, is a colorless gas that supports combustion. It is used as an anesthetic (laughing gas), but for this purpose it is mixed with a proper proportion of oxygen. *Nitric oxide*, NO, is also a colorless gas that combines spontaneously with oxygen to form NO_2. *Nitrogen dioxide*, NO_2, is a brownish-yellow gas formed as above, also when nitric acid is heated. NO_2 combines with itself to form N_2O_4 to a considerable extent at room temperature, and to a greater extent at slightly lower temperatures. *Nitrogen tetroxide*, N_2O_4, is a colorless gas (easily liquefied) that largely decomposes to form NO_2 at or above room temperature. Other oxides of nitrogen are also known.

2. Industrial Uses of Nitric Acid, HNO_3. Large quantities of nitric acid are converted into calcium nitrate and other nitrates for use as fertilizers. One of the largest uses of nitric acid is for the manufacture of high explosives such as nitroglycerin, trinitrotoluene, TNT, picric acid, and nitrocellulose. Certain of these explosives are essential for the blasting operations of quarrying, mining, stump removal, and general construction of all kinds. Dynamite is a mixture of nitroglycerin with a filler such as fuller's earth. Other explosives, such as ammonium nitrate and nitrocellulose, are also usually present in the mixture.

Nitric acid is also used for the production of pyroxylin plastics, which are formed by allowing nitric acid to act on cotton in such a way as to form nitrocellulose containing less nitrogen than gun cotton. Pyroxylin plastics may be sawed, filed, chiseled, punched, pressed, stretched, or molded. They are soft when warm, hard when cool, and are easily cemented together. They are not ordinarily subject to corrosion and are stable over indefinite periods of time. They are used in large quantities as artificial leather for upholstery and bookbinding, in plastic wood, and in cold solders. Rapid-drying paints and lacquers often contain pyroxylin plastics. Large quantities are also used for motion-picture films. Their only disadvantage is a tendency to burn if overheated. Nitric acid is also of importance in the synthesis of dyes and drugs, many of which are nitrogen compounds.

3. Manufacture of Nitric Acid by Oxidation of Ammonia. Ostwald Process. This is accomplished in three reactions. The second and third reactions take place spontaneously but the first one makes use of a platinum catalyst and a temperature of about 400°C.

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O \qquad (1)$$
$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

The NO formed in the third step is mixed with that from the first step in the process.

Exercises

1. A temperature of 500°C. gives a lower yield of NO in reaction (1) than 400°C. Is this action exothermic?

2. Would increase in pressure result in an increase in yield of NO in reaction (1)?

4. Other Methods for the Manufacture of Nitric Acid. At least two other methods have been in use, but are of decreasing importance. The *arc process* forms NO by direct combination of N_2 and O_2 in an electric arc, and the NO is then converted to nitric acid as in the ammonia oxidation process. The *Chile saltpeter process* made use of sodium nitrate and sulfuric acid as described below in connection with the laboratory preparation of nitric acid.

5. Laboratory Preparation of Nitric Acid. Solid sodium nitrate is heated with concentrated sulfuric acid in a glass retort. The products are sodium bisulfate and nitric acid. The sodium bisulfate remains in the retort and the nitric acid distills off. The equation for the above reaction is

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

6. Properties of Nitric Acid. *a.* Nitric acid is an active acid. It ionizes and is neutralized by bases in the usual manner.

b. Like many other acids, nitric acid reacts with alcohols to form esters. This reaction, called *esterification*, is analogous to neutralization. An *alcohol* is a compound of a hydrocarbon radical with the hydroxyl radical, and an *ester* is a compound of a hydrocarbon radical with an acid radical.

Typical examples of esterification are given below.

$C_2H_5OH + HNO_3 \rightarrow C_2H_5NO_3 + H_2O$
ethyl alcohol → ethyl nitrate (an ester)

$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O$
glycerin (an alcohol) → glycerol trinitrate or nitroglycerin (an ester)

$\text{Cellulose} + HNO_3 \rightarrow \text{Cellulose nitrate} + H_2O$
an alcohol → an ester

c. The reaction of nitric acid with metals is unusual because it acts as an oxidizing agent as well as an acid. With iron and less active metals, concentrated nitric acid reacts to produce the metallic nitrate, water, and NO_2. Dilute nitric acid forms NO instead of NO_2. Hydrogen is not generally produced in these reactions. With metals more active than iron it is impossible to give a general rule. For instance, zinc reacts with very dilute nitric acid, producing ammonium nitrate, zinc nitrate, and water. Nitric acid reacts with nonmetals to produce the oxide or acid of the nonmetal, water, and either NO or NO_2.

Illustrative case. Silver with dilute nitric acid.

$Ag + HNO_3 \rightarrow AgNO_3 + NO + H_2O$ (skeleton equation)

Oxidation, loss of e^-
$1e^- \times 3 = 3e^-$

$3Ag^0 + 1H\overset{5+}{N}O_3 \rightarrow 3\overset{+}{Ag}NO_3 + 1\overset{2+}{N}O + H_2O$

Reduction, gain of e^-
$3e^- \times 1 = 3e^-$

Add $3HNO_3$ to provide $3NO_3^-$ to form $3AgNO_3$.

$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$ (balanced equation)

d. Nitric acid has an unusual property in that it is a *nitrating agent.* This property is important in connection with the production of explosives as well as drugs and dyes.

$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
benzene → nitrobenzene

$C_7H_8 + 3HNO_3 \rightarrow C_7H_5(NO_2)_3 + 3H_2O$
toluene → trinitrotoluene (TNT)

$C_6H_5OH + 3HNO_3 \rightarrow C_6H_2(OH)(NO_2)_3 + 3H_2O$
phenol (carbolic acid) → trinitrophenol (picric acid)

Exercises

3. Write the equation for the ionization of nitric acid.

4. Write full ionic equations for the neutralization of nitric acid by (*a*) sodium hydroxide, (*b*) calcium hydroxide, (*c*) aluminum hydroxide, (*d*) ammonium hydroxide, (*e*) one other hydroxide.

5. Write skeleton equations for each of the following (see also Exercise 6): (*a*) silver with dilute nitric acid, (*b*) copper with dilute nitric acid, (*c*) silver with concentrated nitric acid, (*d*) iron with dilute nitric acid (ferric nitrate is formed), (*e*) copper with concentrated nitric acid, (*f*) iron with concentrated nitric acid, (*g*) sulfur with concentrated nitric acid (sulfuric acid is formed), (*h*) carbon with concentrated nitric acid (carbon dioxide is formed), (*i*) phosphorus with concentrated nitric acid (phosphoric acid is formed), (*j*) bismuth with dilute nitric acid, (*k*) zinc with very dilute nitric acid (see Sec. 6*c*), (*l*) ferrous sulfate, sulfuric acid, and dilute nitric acid (ferric sulfate, nitric oxide, and water are formed).

6. Balance each of the above equations by use of the valence change, electron method (see illustrative case, also XI. 10). Carry out the following preliminary steps:

a. Be sure that all formulas in skeleton equations are correct.

b. Mark the valence of the elements that change in valence.

c. Mark the electrons gained and lost, and use these to balance the equations.

7. Mark oxidation and reduction and *total* electrons gained and lost in each of the above equations.

8. Starting with nitrogen from liquid air, write five equations showing the following conversion processes:

$$N_2 \rightarrow NH_3 \rightarrow NO \rightarrow NO_2 \rightarrow HNO_3 \rightarrow C_3H_5(NO_3)_3.$$

EXPLOSIVES

7. The use of explosives in excavating, mining, and quarrying operations has already been mentioned. About 190,000 tons of explosives are used annually for such purposes in the United States. Explosives may be regarded as most useful tools of the engineer, the farmer, and the sportsman. Unfortunately for the human race, explosives have been used for military purposes. The destructive effects of bombs, rifle bullets, shrapnel, and torpedoes are only too well known to both soldiers and civilians.

8. General Characteristics of Explosives. An explosive may be defined as a substance that will produce a large volume of gaseous products by a very rapid reaction.

a. Effectiveness. It is the tremendous expansive force of the gases formed that produces the useful or harmful effect as the case may be. For example, nitroglycerin decomposes during explosion, according to the following equation:

$$4C_3H_5(NO_3)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

Exercises

9. From the above equation calculate (*a*) the total number of moles of gases formed per mole of nitroglycerin, (*b*) the total number of liters of gases (at S.C.) formed per gram of nitroglycerin, (*c*) the total number of liters of gases (at 2200°C.) formed per gram of nitroglycerin.

NOTE: In (*b*) use the G.M.V. principle.

10. In a single blast in a limestone quarry, 125,000 tons of limestone were brought down by 26,500 lb. of dynamite (data from Hercules Powder Company). Calculate the number of tons of limestone brought down per pound of dynamite used.

b. Stability. It is a well-known fact that rifle cartridges and dynamite can be stored and transported safely if properly handled. In fact, millions of pounds of explosives have been transported by railroads without serious accident during the past 15 years. The high explosive in a cannon shell will not explode even under the impact of the firing charge, until the shell hits the target. It is essential, however, that dynamite and other industrial explosives be handled with proper precautions and only by experienced workers. For example, exothermic decomposition of dynamite may begin at a temperature of 150°C. At 200 to 300°C. most explosives will explode instantaneously. Mechanical impact by tools or rock should be avoided.

9. Important Types of Explosives. *a. Black Powder.* This is the oldest type of explosive, having been discovered by Roger Bacon in England in the thirteenth century. The Chinese have also used it from very early times. Three materials, charcoal, sulfur, and sodium nitrate or potassium nitrate, are used in its manufacture. These materials, after thorough mixing in the moist condition, are converted into granules. The granules are then glazed with graphite. Black powder is a burning type of explosive. During the explosion, the sulfur and the charcoal unite with oxygen of the sodium nitrate or potassium nitrate. The gaseous products of the combustion are carbon dioxide, carbon monoxide, sulfur dioxide, and nitrogen. Numerous solid products are also produced which form smoke and cause the fouling of rifle barrels.

b. Smokeless Powder. The principal ingredient of smokeless powder is cellulose nitrate (Sec. 6) which is made by treatment of cotton or wood pulp with a mixture of strong nitric acid and sulfuric acid. The sulfuric acid removes the water formed in the reaction. The nitric acid introduces nitrate radicals which furnish oxygen for the combustion of the carbon and the hydrogen. The products of the combustion (explosion) are carbon monoxide, carbon dioxide, nitrogen, and water vapor. The combustion, however, is much more rapid than in the case of black powder since the oxygen is in the same molecule, whereas in black powder the oxygen of the potassium nitrate unites with the carbon and the sulfur, which are separate components of the mixture.

Cellulose nitrate, when used alone, burns so rapidly that it is not suitable for ammunition. It is, therefore, dissolved in acetone or in a mixture of alcohol and ether. In this form it is extruded from a die and cut into small rod-shaped grains of uniform size. The solvent is largely removed by evaporation.

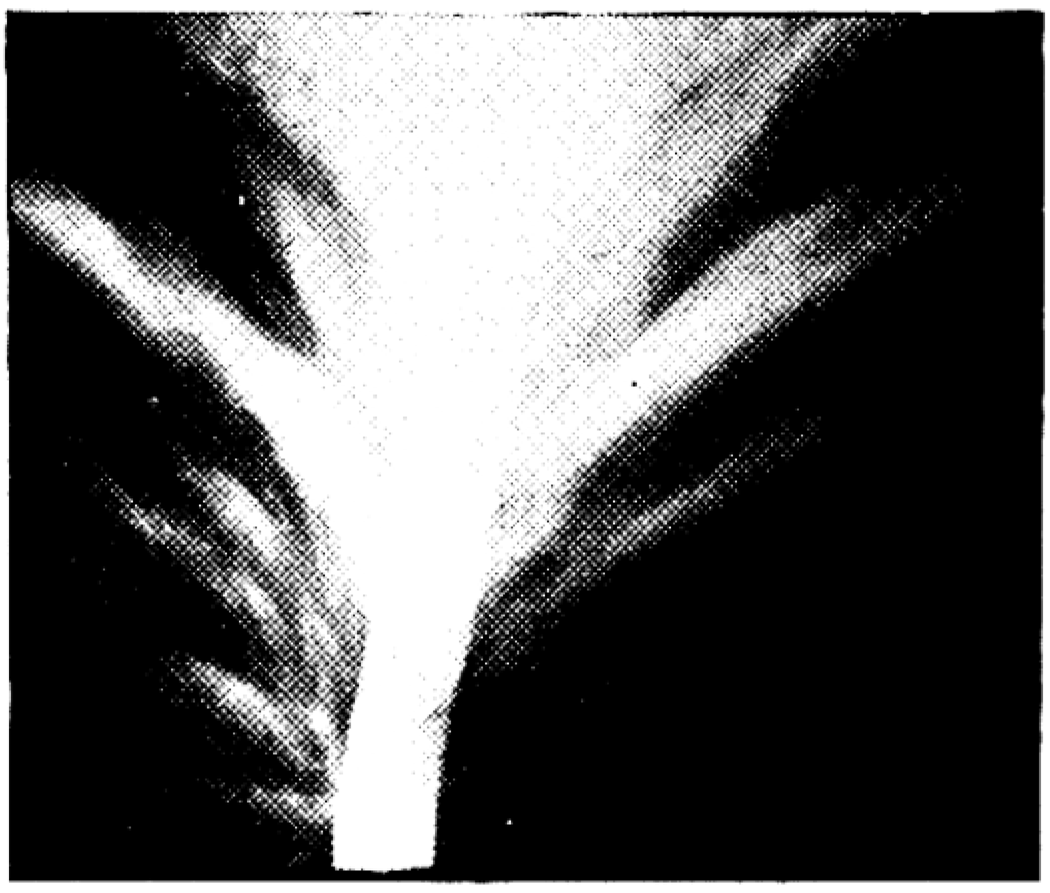

FIG. 1. Explosion photograph of a dynamite cartridge. (*J. Chem. Education and Hercules Powder Company.*)

Two types of smokeless powder (single base and double base) are manufactured. The single-base type contains only cellulose nitrate. The double-base type contains cellulose nitrate and nitroglycerin.

The term *smokeless powder* is not a strictly accurate one as evidenced by the fact that large volumes of smoke are produced by it when fired in large quantities, as in battleship guns.

c. Nitroglycerin and Dynamite. Nitroglycerin is an unstable liquid. When mixed with about 8 per cent of cellulose nitrate, it forms blasting gelatin, which is used extensively in the blasting of oil wells. *Dynamite* is composed of nitroglycerin, an absorbent material (*e.g.*, wood pulp), and an oxidizing material, usually sodium nitrate or ammonium nitrate. The combustion of wood contributes heat and energy in the explosion of the dynamite. The mixture is usually sold in the form of small cylindrical "sticks" covered with waxed paper.

Dynamites containing ammonium nitrate are employed extensively for blasting in mines. It is estimated that ammonium nitrate makes up about 40 per cent of all industrial explosives used. This fact illustrates clearly the great importance of ammonia and nitric acid in the explosive industry.

d. Trinitrotoluene TNT. Toluene, C_7H_8, is produced by the fractional distillation of coal tar and from petroleum. When it reacts with nitric acid, three nitro groups are introduced in the place of three hydrogen atoms (Sec. 6).

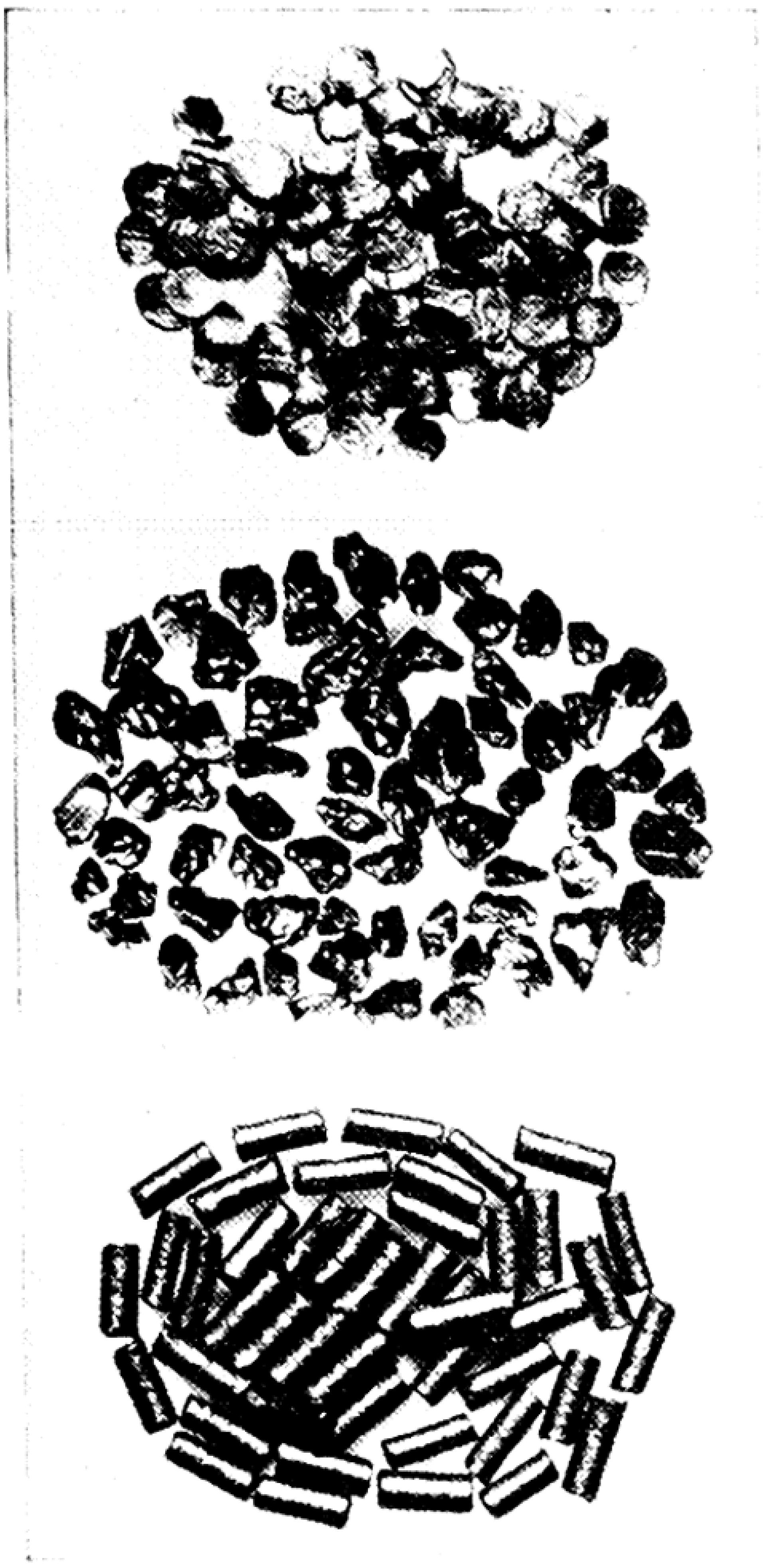

FIG. 2. Three types of powder. *Top:* smokeless powder for shotgun; *middle:* black powder for shotgun; *bottom:* smokeless powder for rifle. (*J. Chem. Education and Hercules Powder Company.*)

The bursting charge of shells, bombs, and torpedoes is usually trinitrotoluene mixed with ammonium nitrate. This mixture is very stable but, when detonated, it explodes with extreme speed and violence. The use of trinitrotoluene as a propellent charge in a gun would rupture the barrel of the gun. For this reason, the propellent charge in cannon shells is smokeless powder which develops less pressure and shock in the gun.

e. Detonators. Black powder explodes when ignited by a fuse containing combustible substances. Dynamite and other high explosives, however, are set off by means of *detonation* or shock induced by the explosion of small charges of mercuric fulminate, $Hg(CNO)_2$, lead azide, $Pb(N_3)_2$, or organic explosives. The detonator charge is enclosed in a small metal container (cap) which is placed in close contact with the explosive to be used. In guns, the cap is exploded by the mechanical impact of the firing pin. In blasting caps, the cap is exploded by an electric current sent through it from a battery, or by sparks from a fuse.

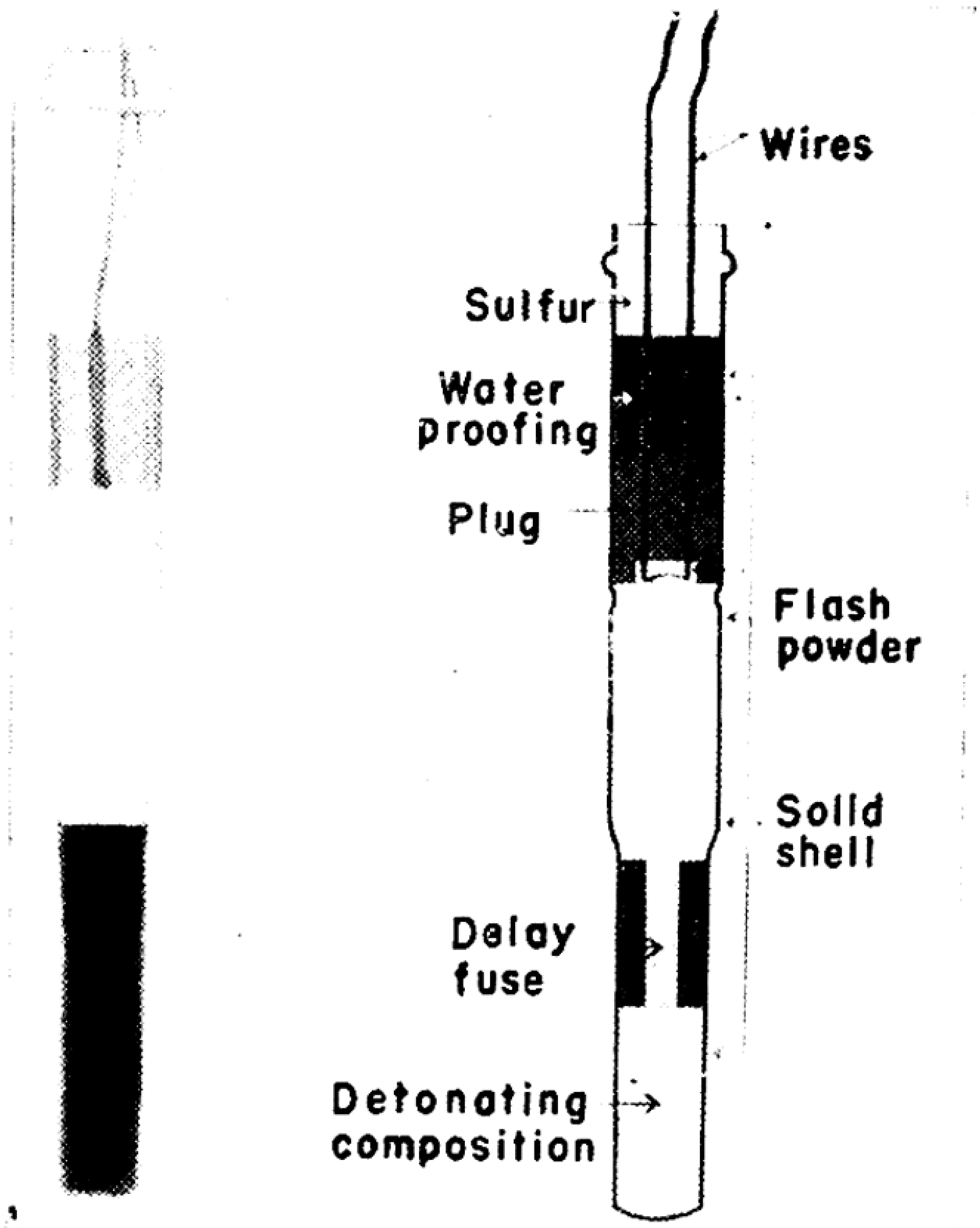

FIG. 3. Electric blasting cap. Left: X-ray photograph; right: diagram. (*J. Chem. Education and Hercules Powder Company.*)

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CHAPTER XX

PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH. FERTILIZERS

In the preceding chapter, we have learned that nitrogen forms a number of oxides and that nitric acid is a strong oxidizing agent. The variable valence of nitrogen is an important fundamental property in the study of nitrogen and the other elements of the nitrogen family. These elements constitute Group V of the periodic table. (XVI, 2).

1. The Nitrogen Family. This includes the elements nitrogen, phosphorus, arsenic, antimony, and bismuth. Table I summarizes essential information concerning them and provides an excellent example of increasing metallic nature with increasing atomic weight.

TABLE I

Symbol	Atomic weight	Description	Common valences
N	14	Colorless gas	+5, +3, −3
P	31	Red or white solid	+5, +3, −3
As	75	Metallic appearing solids	+5, +3, −3
Sb	122		+5, +3, (−3)
Bi	209		+3

Table II summarizes the formulas and names of the more important compounds of phosphorus, arsenic, antimony, and bismuth. Numerous rare and relatively unimportant compounds have been omitted.

TABLE II

Trioxides: N_2O_3, nitrogen trioxide; P_2O_3, phosphorus trioxide; As_2O_3; Sb_2O_3; Bi_2O_3

Pentoxides: N_2O_5, nitrogen pentoxide; P_2O_5; As_2O_5

Acids derived from trioxides: HNO_2, nitrous acid; H_3PO_3, phosphorus acid; H_3AsO_3, arsenious acid

Acids derived from pentoxides: HNO_3; H_3PO_4; H_3AsO_4, arsenic acid

Salts: Salts of HNO_2 contain NO_2 radical and are called *nitrites*
Salts of H_3PO_3 contain PO_3 radical and are called *phosphites*
Salts of H_3AsO_3 contain AsO_3 radical and are called *arsenites*
Salts of H_3PO_4 contain PO_4 radical and are called *phosphates*
Salts of H_3AsO_4 contain AsO_4 radical and are called *arsenates*

Chlorides: PCl_3, phosphorus trichloride; PCl_5, phosphorus pentachloride; $AsCl_3$; $AsCl_5$; $SbCl_3$; $BiCl_3$; SbOCl, antimony oxychloride (antimonyl chloride); BiOCl, bismuth oxychloride

Sulfides: As_2S_3, arsenic trisulfide (arsenious sulfide); As_2S_5, arsenic pentasulfide; Sb_2S_3; Sb_2S_5; Bi_2S_3

Miscellaneous compounds: PH_3, phosphine; AsH_3, arsine; $Bi(NO_3)_3$, bismuth nitrate; $BiONO_3$, bismuth subnitrate; $KSbOC_4H_4O_6$, potassium antimony tartrate (tartar emetic)

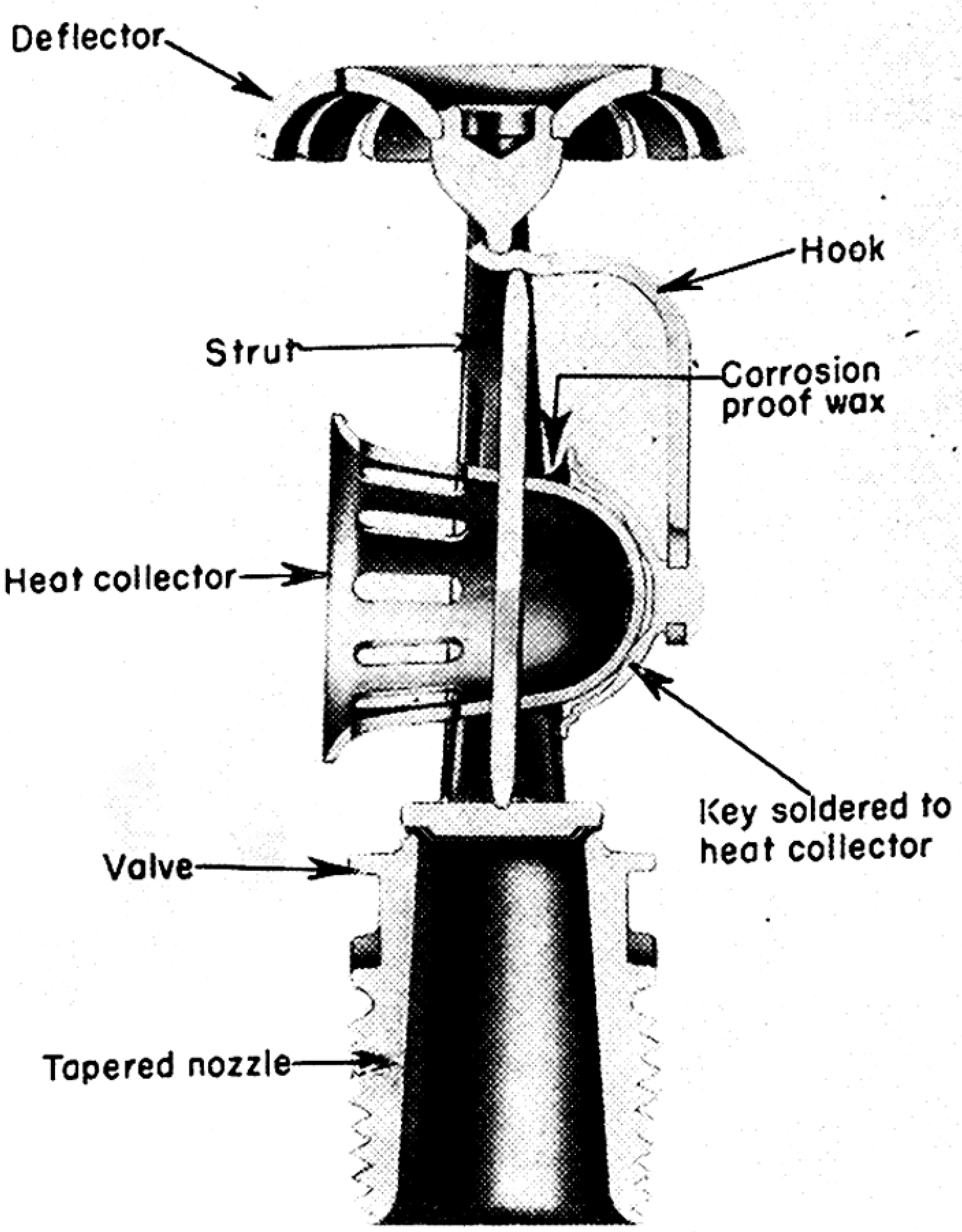

Fig. 1. Fire sprinkler—fusible-alloy type (sectional view). (*Grinnell Company.*)

Exercises

1. Write formulas and names of the five oxides of nitrogen.

2. Write formulas and names for the sodium and calcium salts of each of the above acids.

3. Make a general statement concerning the relation of valence to the names of the acids and salts of the above elements.

2. Uses of the Free Elements P, As, Sb, and Bi. Red phosphorus is used on safety match boxes; white phosphorus is used in incendiary and smokescreen bombs and in rat poisons. Arsenic is used to harden soft alloys, particularly lead shot; also in alloys that expand upon solidification. This property is desirable in type metal to bring out the fine details of the mold. Antimony is used more often than arsenic for this purpose. Antimony is also used in antifriction alloys (bearing metal, babbit metal). Bismuth is used to prepare alloys of unusually low melting point for use in automatic fire-control devices.

3. Uses of Compounds of P, As, Sb, Bi. Various calcium phosphates are regularly used in large quantities in the preparation of commercial fertilizers. Phosphorus trisulfide, P_4S_3, is used in matches. It ignites almost as easily as phosphorus itself. Various arsenites and arsenates, $Cu_3(AsO_3)_2$, $Ca_3(AsO_4)_2$, are important insecticides. Arsenic trioxide is used in glass manufacture to reduce the green or brown tinge in glass due to the presence of impurities (iron) in the glass sand. Antimony trisulfide is used in matches and fireworks. Bismuth subnitrate, $BiONO_3$, is used as a medicine in certain stomach disorders. Numerous other arsenic, antimony, and bismuth compounds are used as drugs and medicines.

4. Basic Salts of Bismuth and Antimony. When a solution of bismuth chloride is diluted with water, a white precipitate appears in the solution, owing to the reaction of water with the $BiCl_3$.

$$BiCl_3 + 2H_2O \rightarrow \underset{\substack{\text{white}\\ \text{precipitate}}}{Bi(OH)_2Cl \downarrow} + 2HCl$$

$$Bi(OH)_2Cl \rightarrow H_2O + \underset{\substack{\text{bismuth}\\ \text{oxychloride}}}{BiOCl \downarrow}$$

Compounds such as $Bi(OH)_2Cl$ and $BiOCl$ are referred to as *basic salts* since they are salts that contain OH radical (as in a base) or O (as in a basic oxide) in their molecules. The first reaction above is a special type of hydrolysis reaction. Bismuth nitrate and antimony trichloride also undergo hydrolysis, forming $BiONO_3$ and $SbOCl$, respectively.

Exercises

4. Write equations for the formation of $BiONO_3$ and $SbOCl$ by hydrolysis.

5. The presence of a considerable amount of HCl in a $BiCl_3$ solution prevents the formation of BiOCl when water is added. Explain this fact in terms of the characteristics of chemical equilibrium (VIII. 3).

5. Sulfides of Arsenic, Antimony, and Bismuth. These compounds are of interest in qualitative analysis procedures involving tests for these elements. The trisulfides are, respectively, yellow, orange, and dark brown and are formed by passing H_2S gas into solutions containing compounds of the elements.

Exercise

6. Write (*a*) molecular, (*b*) full ionic, (*c*) simple ionic equations for the reaction of H_2S with $AsCl_3$, with $SbCl_3$, and with $Bi(NO_3)_3$.

6. Phosphorus. This element never occurs in nature in the free state; its compounds, however, are quite common. Tertiary calcium phosphate, $Ca_3(PO_4)_2$, occurs in the bones and teeth of animals and is an important component of bone black and bone ash. It also occurs in extensive natural deposits as phosphate rock. Proteins (compounds of C, H, O, N, S, P) are present in foods and in muscle, nerve, and brain tissue. Phosphorus is produced commercially in the free state by heating phosphate rock, sand, SiO_2, and coke, C, to a high temperature in a blast furnace or electric furnace. The free phosphorus distills from the other materials and is collected under water. The reaction in the furnace is shown by the equation,

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + 10CO + P_4 \uparrow$$

Phosphorus occurs in two common allotropic forms. Red phosphorus is nonpoisonous and will not catch fire in air unless heated. It is considerably less active than white or yellow phosphorus, which is a dangerous poison and is spontaneously flammable. Both forms of phosphorus burn in an excess of air, forming the pentoxide. Phosphorus is used in matches because the heat and pressure caused by friction in striking the match convert some red phosphorus to the white form. This form begins to oxidize spontaneously, and the heat liberated in this reaction starts the oxidation of the phosphorus sulfide by the PbO_2 or other oxidizing agent in the match head. The heat thus liberated then ignites the rest of the match.

Exercises

7. Which form of phosphorus is used in incendiary bombs and why?

8. Write equations for (*a*) the burning of phosphorus, (*b*) the reaction of phosphorus pentoxide with water, forming H_3PO_4.

7. Ions from Phosphoric Acid. Phosphoric acid forms three different ions as indicated in the following equations:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

Primary phosphate ion forms primary phosphate salts.

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$$

Secondary phosphate ion forms secondary phosphate salts.

$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$

Tertiary phosphate ion forms tertiary phosphate salts.

8. Salts of Phosphoric Acid. Three series of salts are formed. Primary phosphate contain the H_2PO_4 radical; secondary salts, the HPO_4 radical; tertiary salts, the PO_4 radical. For example:

NaH_2PO_4	(primary sodium phosphate or monosodium phosphate)
Na_2HPO_4	(secondary sodium phosphate or disodium phosphate)
Na_3PO_4	(tertiary sodium phosphate or trisodium phosphate)
$Ca(H_2PO_4)_2$, or $CaH_4(PO_4)_2$	(primary or monocalcium phosphate)
$CaHPO_4$, or $Ca_2(HPO_4)_2$	(secondary or dicalcium phosphate)
$Ca_3(PO_4)_2$	(tertiary or tricalcium phosphate)

Exercises

9. Write formulas and names for the three phosphates of (*a*) potassium, (*b*) ammonium, (*c*) magnesium.

10. Write formulas and names for three sodium salts of arsenic acid.

9. Tests for Phosphate Salts. The standard test for the phosphate ion, PO_4^{---}, in solution is the formation of a yellow precipitate of *ammonium phosphomolybdate* when ammonium molybdate, $(NH_4)_2MoO_4$, is allowed to react with the phosphate salt solution. It is necessary that nitric acid be present in the mixture and that an excess of ammonium molybdate be used. The yellow precipitate forms slowly unless the solution is boiled. Solutions containing the arsenate ion, AsO_4^{---}, undergo a similar reaction except that boiling is necessary in order to form the yellow precipitate. Phosphates also form a yellow precipitate with $AgNO_3$ solution.

$$Na_3PO_4 + 3AgNO_3 \rightarrow Ag_3PO_4 \downarrow + 3NaNO_3$$

This precipitate is easily soluble in nitric acid; in fact, it will fail to form if the test is carried out in an acid solution. Arsenates behave similarly, but the precipitate formed is chocolate brown in color.

FERTILIZERS

10. General. A fertilizer is generally regarded as any material that is added to the soil in order to increase plant growth. The value of animal manures as fertilizers has been known for centuries, but it is only within recent times (since 1860) that chemical or commercial fertilizers have been utilized. Commercial fertilizers usually contain definite and guaranteed amounts of nitrogen, phosphorus, listed as

P_2O_5, and potassium, listed as potash, K_2O. Other elements, *e.g.*, boron, copper, and manganese, also stimulate plant growth and are included in certain brands of commercial fertilizers. Lime, CaO, is used as a direct fertilizer for wheat and other similar crops, and as an indirect fertilizer or soil amendment to improve the physical and chemical conditions of the soil (see Sec. 11).

Exercise

11. Would it be advisable to apply lime with ammonium sulfate? Explain.

Fertilizer plot tests are conducted by the state experiment stations and by fertilizer manufacturers in order to determine the exact fertilizer requirements of the various crops and soils.

11. Classification of Fertilizers.[1]

I. Direct fertilizer
  A. Nitrogenous fertilizers
    1. Organic
      a. Animal
        Dried blood, tankage, fish scrap, manures
      b. Vegetable
        Straw, muck, peat, cover crops, cottonseed meal, etc.
    2. Inorganic (or mineral)
      Sodium nitrate, ammonium sulfate, calcium cyanamide, etc.
  B. Phosphate fertilizers
    1. Organic
      Farm manures, guano
    2. Inorganic
      Rock phosphate, superphosphate or acid phosphate, bones
  C. Potash fertilizers
    1. Organic
      Tobacco waste, farm manures, kelp
    2. Inorganic
      Potassium chloride, potassium sulfate, wood ashes
  D. Calcium fertilizers
    1. Inorganic
      Quicklime, hydrated lime, limestone, gypsum
II. Indirect fertilizer or amendment
  A. Organic
    Green cover crops, leaf mold, etc.

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[1] Hedges and Brayton, "The Applications of Chemistry to Agriculture," Chap. IX, D. Appleton-Century Company, Inc., New York, 1938.

B. Inorganic
Calcium compounds (see I, *D*)
Salt, iron compounds

12. Phosphate Fertilizers. In order to be useful as a fertilizer, a compound must be soluble in water. Insoluble compounds are not available, since only solutions can pass through the root walls of plants. Tertiary calcium phosphate, $Ca_3(PO_4)_2$, occurs in huge quantities in natural deposits, but it is of little immediate value as a fertilizer because it is insoluble in water. Secondary calcium phosphate, $CaHPO_4$, is somewhat more soluble. Primary calcium phosphate, $Ca(H_2PO_4)_2$, is quite soluble and so is readily available to plants as a fertilizer material. Large amounts of tertiary calcium phosphate are converted to primary phosphate by reaction with sulfuric acid.

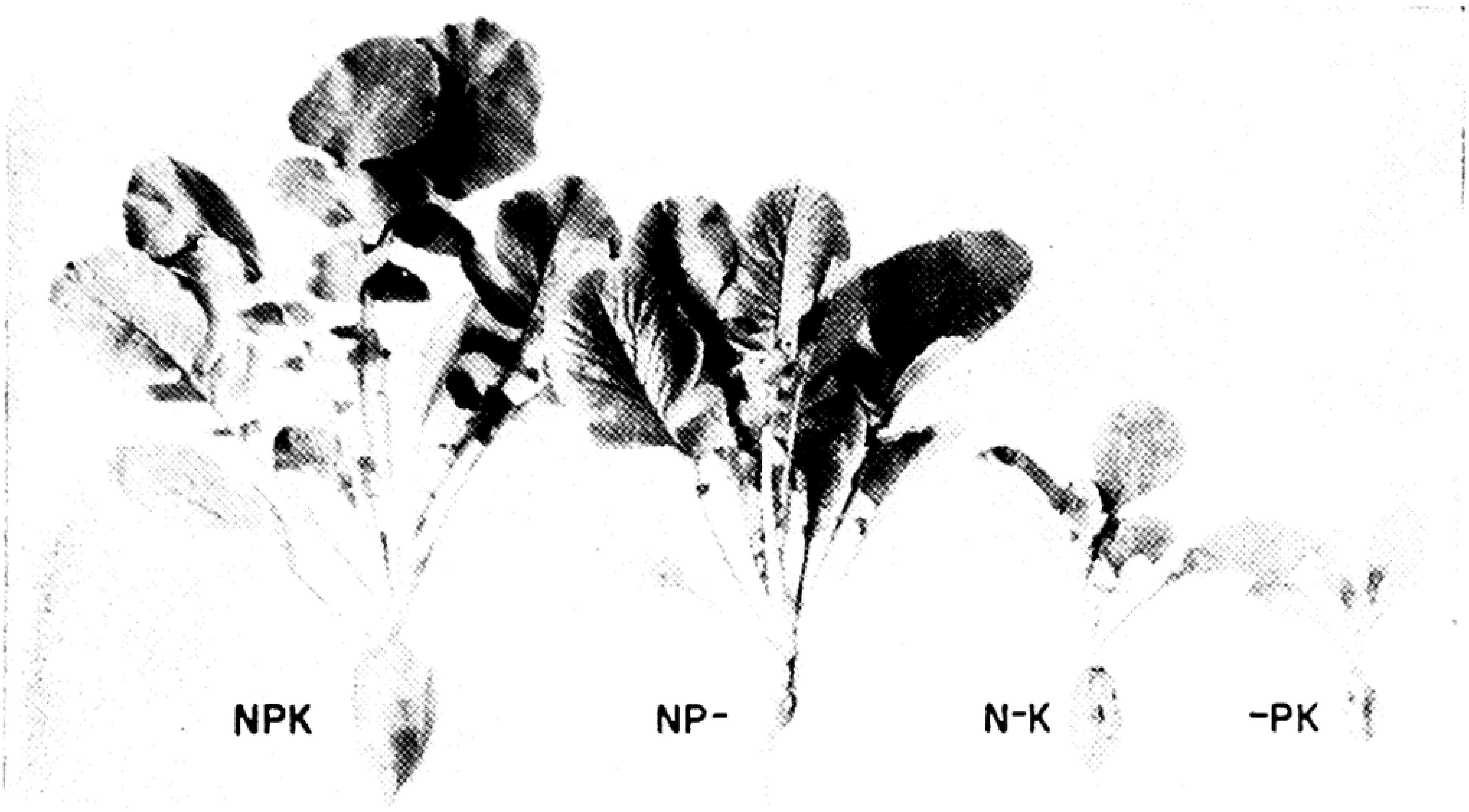

FIG. 2. Influence of nitrogen, phosphorus, and potassium in plant growth. Potash is needed to fill out the radish (NP-); phosphorus (N-K) and nitrogen (-PK) are needed for foliage growth. (*Courtesy of American Potash Institute, Inc.*)

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

The resulting mixture of the primary phosphate and calcium sulfate is known as *superphosphate* or *superphosphate of lime*. Some secondary and tertiary phosphate may also be present in the mixture. The tertiary calcium phosphate (1 to 2 per cent) serves to keep the mixture dry and in good mechanical condition. It may also react with primary phosphate and produce secondary or "reverted" phosphate.

13. Fertilizer Formulas. Commercial fertilizers are referred to as 4-8-4, 4-12-8, etc. These three numbers refer to the amounts of nitrogen, phosphorus pentoxide, and potassium oxide present—always in the order N-P-K. Thus, a 4-8-4 analysis indicates 4 per cent N, 8 per cent P_2O_5 (not 8 per cent phosphorus), and 4 per cent K_2O.

It should be noted that since 1 molecule of $Ca_3(PO_4)_2$ contains 2 atoms of phosphorus, it is chemically equivalent to 1 molecule of P_2O_5, which also contains 2 atoms of phosphorus. This relationship is expressed as follows:

$$\begin{array}{ccccc} 1Ca_3(PO_4)_2 & \Bumpeq & 2P & \Bumpeq & 1P_2O_5 \\ 310\text{ g.} & & 62\text{ g.} & & 142\text{ g.} \end{array}$$

Since 310 g. $Ca_3(PO_4)_2$ contains enough phosphorus to form 142 g. P_2O_5, it is evident that the percentage of P_2O_5 in $Ca_3(PO_4)_2$ is

$$^{142}/_{310} \times 100 = 45.8\%\ P_2O_5$$

By a similar method it can be shown that

$$\begin{array}{ccccc} 1CaHPO_4 & \Bumpeq & 1P & \Bumpeq & \tfrac{1}{2}P_2O_5 \\ 136\text{ g.} & & 31\text{ g.} & & 71\text{ g.} \end{array}$$

so that the percentage of P_2O_5 in $CaHPO_4$ is

$$^{71}/_{136} \times 100 = 52.2\%\ P_2O_5$$

Exercises

12. Calculate the percentage of P_2O_5 in pure (*a*) $Ca(H_2PO_4)_2$, (*b*) Na_2HPO_4, (*c*) KNH_4HPO_4, (*d*) $Mg_3(PO_4)_2$.

13. A fertilizer analysis is given as 8 per cent P_2O_5. What is the actual percentage of phosphorus?

14. A fertilizer consists of 20 per cent tertiary calcium phosphate, 15 per cent primary calcium phosphate, and the remainder inert filler. Calculate (*a*) the total phosphorus content and (*b*) the available phosphorus content. Express the results as percentage of P_2O_5.

15. Calculate the NPK percentage analysis of a fertilizer composed of the following mixture:

300 lb. sodium nitrate	15% N
350 lb. dried blood	10% N
1,000 lb. superphosphate	16% P_2O_5
240 lb. sulfate of potash	50% K_2O
110 lb. filler	
2,000 lb. total weight	

NOTE: Calculate (1) the total number of pounds of N in the mixture; thus,

$$\begin{array}{rcl} 300\text{ lb.} \times {}^{15}/_{100} & = & 45\text{ lb. N} \\ 350\text{ lb.} \times {}^{10}/_{100} & = & 35\text{ lb. N} \\ \text{Total}\ldots\ldots\ldots\ldots & & \overline{80\text{ lb. N}} \end{array}$$

(2) the total per cent of N in 2,000 lb., thus,

$$\frac{80}{2{,}000} \times 100 = 4\% \text{ N}$$

In a similar manner, calculate the percentage of P_2O_5 and of K_2O.

14. Insecticides (Inorganic). By inspection of Table II it will be noted that the oxides, the acids, and the salts of arsenic are similar to those of phosphorus. For review, these compounds are again listed below. Name each compound.

As_2O_3	H_3AsO_3	$Ca_3(AsO_3)_2$
As_2O_5	H_3AsO_4	$Ca_3(AsO_4)_2$

Arsenic compounds are used extensively in the preparation of insecticides because they are very poisonous to insects. White arsenic, As_2O_3, arsenate of lime, $Ca_3(AsO_4)_2$; and arsenate of lead, $Pb_3(AsO_4)_2$, are common preparations. Nearly 70,000,000 lb. of the arsenates of lime and of lead are used annually in the United States, particularly in the cotton areas of the South as a control for the cotton weevil. *Paris green* is a complex material containing copper acetate with varying percentages of As_2O_3. Other well-known inorganic insecticides are calcium fluoride, calcium oxide, sulfur, and *Bordeaux mixture*, $CuSO_4$ and $Ca(OH)_2$.

SUGGESTED READING

Killefer, What's New in Phosphorus? *Ind. Eng. Chem.*, 30, 967 (1938).
Easterwood, Recent Developments in the Phosphate Field, *Ind. Eng. Chem.*, 34, 13 (1942).

CHAPTER XXI

CARBON AND ITS OXIDES. FUELS

Carbon is a constituent element in all plant and animal materials, as well as in coal and petroleum. Alcohol, ether, gasoline, sugar, starch, and many other important materials also contain carbon. It is, therefore, an extremely important element.

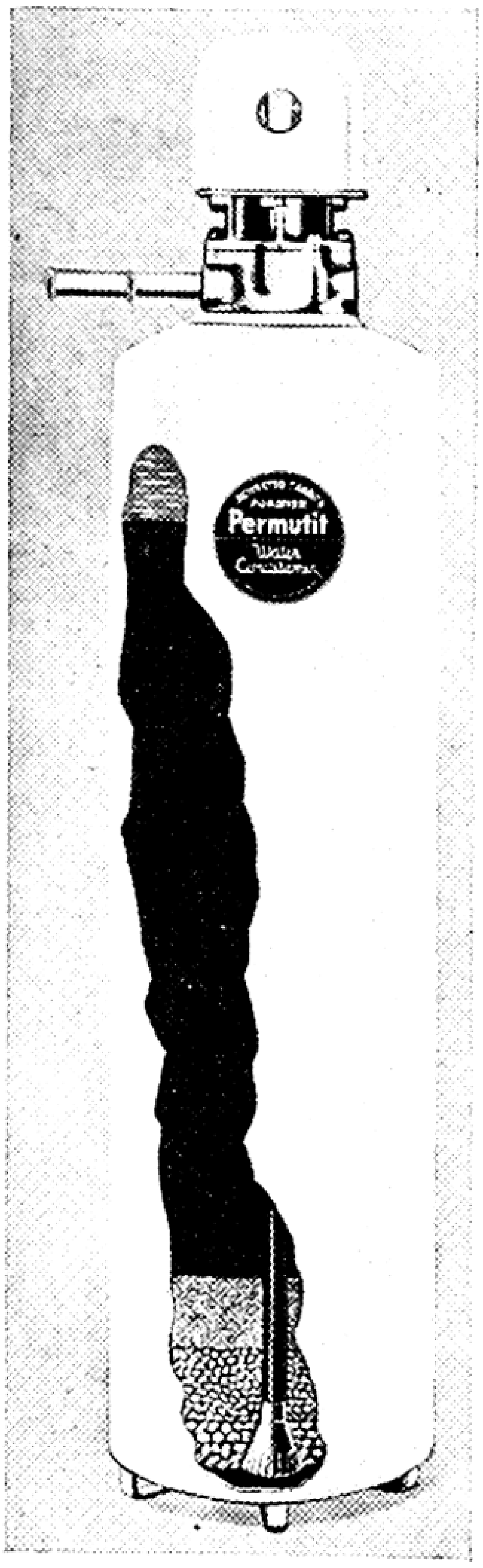

FIG. 1. Activated carbon water-conditioner. (*The Permutit Company.*)

1. Natural and Prepared Forms of Carbon. Diamond and graphite are natural *allotropic* forms of carbon. Each form has a definite arrangement of carbon atoms to which the properties of these materials are definitely related. Synthetic diamonds have been produced but not on a practical scale.

Charcoal, coke, lampblack, carbon black, and graphite are forms of carbon, commonly produced by industrial methods, and contain impurities. Bone black contains carbon and a large proportion of calcium phosphate.

Some of the uses of these various forms of carbon are common knowledge. Considerable quantities of black diamonds are used on drill points, and diamond dust is regularly used as the abrasive when very hard materials are to be ground or drilled. Diamonds are harder than any synthetic abrasive. Finely powdered anthracite coal is being used in considerable quantities as a filtering medium to replace sand filters in water purification plants. Specially prepared forms of charcoal are of importance in removing the brown color from raw sugar and in decolorizing or deodorizing water and numerous other materials. The charcoal has the property of *adsorbing* the colored or odoriferous material. This same property allows the use of charcoal in gas-mask canisters since the carbon adsorbs the poisonous gases and makes the air safe for respiration. Carbon black is used in considerable quantities in rubber automobile tires and greatly increases their life. It is also used in making the special inks used on high-speed printing presses. Carbon black is made by allowing a fan-shaped luminous natural gas flame to impinge upon a moving steel plate. The carbon black thus deposited is removed by a scraper and automatically collected.

Exercise

1. Name two other elements existing in allotropic forms.

2. Electric Furnace Products Containing Carbon. Electric furnaces used in carrying on chemical reactions are of two types: (*a*) the arc type, (*b*) the resistance type. In both, the sole function of the electricity is to produce a sufficiently high temperature for the desired reaction. In the resistance type of furnace, the high temperature is produced by passing such a heavy current through carbon that the carbon becomes incandescent. The necessary materials are either mixed with the carbon or placed adjacent to it so that they also become hot. In the arc-type furnace, the reacting materials are merely brought near or actually into the arc and are thus heated to approximately 3000°C.

Calcium carbide, CaC_2, is an example of a substance prepared on a large scale in an arc-type electric furnace according to the following equation:

$$CaO + 3C \rightarrow CaC_2 + CO$$

This substance, when allowed to react with water, forms acetylene, C_2H_2, a gaseous fuel used in the oxyacetylene welding torch.

Carborundum or silicon carbide, SiC, an abrasive, is an example of a substance prepared in a resistance-type furnace (XXIV. 8).

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

3. Carbonic Acid, Carbonates, and Bicarbonates. Carbon dioxide is the acid anhydride of carbonic acid, which is definitely unstable, and is a weak acid which forms two series of salts: the normal carbonates characterized by the CO_3 (valence of 2) radical and the bicarbonates by the HCO_3 (valence of 1) radical.

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \xleftarrow{\rightarrow} H^+ + HCO_3^- \xleftarrow{\rightarrow} H^+ + CO_3^{--}$$

Exercises

2. Give the names and formulas of three other oxides that are acid anhydrides. Write equations similar to that above showing the formation and the ionization of the corresponding acids.

3. By the use of long and short arrows indicate which of the acids above are weak and which are strong (IX. 12).

4. State the effect of (*a*) heat and (*b*) increase in pressure in the reaction of CO_2 with water.

5. Write formulas for normal ammonium carbonate, ammonium bicarbonate, magnesium carbonate, ferrous carbonate, ferrous bicarbonate.

The most common and useful carbonates are as follows:

$Na_2CO_3 \cdot 10H_2O$ . . .	Washing soda	Normal sodium carbonate used in water softening and the manufacture of glass
Na_2CO_3	Soda ash	
$NaHCO_3$	Baking soda or sodium bicarbonate	
$CaCO_3$	Limestone, calcite, or calcium carbonate	
$Ca(HCO_3)_2$	Calcium bicarbonate, present in most ground waters	

4. Carbon Dioxide. Carbon dioxide occurs in a small but essential proportion in the atmosphere. It is also present in all natural waters and in some natural and volcanic gases.

Carbon dioxide is formed by combustion, decay, respiration, or fermentation, by the reducing action of CO or C on an oxide, or by the decomposition of carbonates by heat or by means of acids. In order to produce carbon dioxide by combustion or decay, an excess of oxygen (air) must be present.

Compounds of C, H, O generally burn to CO_2 and H_2O during combustion in sufficient air or oxygen. Any carbon compound produces CO_2 when it decays in an atmosphere of air or oxygen. During ordinary fermentation, sugar or starch is converted into alcohol and carbon dioxide.

All carbonates and bicarbonates (except sodium and potassium carbonates) decompose upon heating. Bicarbonates produce normal carbonates, water, and carbon dioxide. Carbonates produce a metallic oxide and carbon dioxide. All carbonates are decomposed by acids producing carbonic acid which is unstable.

$$CaCO_3 + 2HCl \rightarrow H_2CO_3 + CaCl_2$$
$$H_2CO_3 \rightarrow H_2O + CO_2\uparrow$$

Exercises

6. Write the equation for the formation of CO_2 from (*a*) C, (*b*) CO, (*c*) $C_{12}H_{22}O_{11}$ (sugar) by combustion.

7. Write equations for the effect of heat upon (*a*) calcium carbonate, (*b*) magnesium carbonate, (*c*) copper carbonate, (*d*) sodium bicarbonate, (*e*) calcium bicarbonate.

8. Write equations for the decomposition, by acids, of the carbonates listed in Exercise 7. Use a different acid for each carbonate.

5. Physical Properties of Carbon Dioxide. Carbon dioxide is somewhat unusual in that upon cooling at ordinary pressure it changes directly to the solid state. Solid CO_2 is called *dry ice.* Liquid CO_2 exists only under considerable pressure. Solid CO_2 is in equilibrium with CO_2 vapor at atmospheric pressure at −78°C., and this is the lowest temperature attained in ordinary dry-ice refrigeration. It is a colorless, odorless gas.

Exercises

9. Calculate the density of CO_2 relative to (*a*) air, (*b*) CO, (*c*) O_2, (*d*) N_2, (*e*) H_2.

10. State the color, taste, and solubility of CO_2 (from experiments).

11. Explain why soda water and other carbonated liquids foam or effervesce when freshly drawn. (Consider the effect of change of pressure.)

6. Chemical Properties of Carbon Dioxide. Carbon dioxide is exceptionally stable toward heat, and yields its oxygen to other substances only in unusual cases and at high temperatures. Carbon dioxide does not support combustion under all ordinary conditions.

Exercises

12. Write equations for the reactions of (*a*) hot carbon with CO_2. This reaction produces CO and occurs in the interior of a bed of burning coke. (*b*) CO_2 with water to form carbonic acid (see Sec. 3). (*c*) CO_2 with $Ca(OH)_2$. A milky precipitate of calcium carbonate is formed. This reaction is commonly used as a test for CO_2. CO_2 reacts with other bases in a similar manner.

13. Write equations for the reaction of CO_2 with (*a*) KOH, to form $KHCO_3$; (*b*) KOH to form K_2CO_3; (*c, d*) NaOH (2 equations), (*e*) $Ca(OH)_2$ to form $Ca(HCO_3)_2$.

Probably the most important chemical property of CO_2 is its reaction with water in photosynthesis in plants (XXIII. 2).

$$6CO_2 + 5H_2O \rightarrow \underset{\text{starch or cellulose}}{(C_6H_{10}O_5)_x} + 6O_2$$

7. Physiological Effects of Carbon Dioxide. It is added in small amounts to the oxygen used in hospitals as an aid to respiration. The CO_2 seems to exert a stimulating effect on the nerve centers in the brain, controlling respiration. Gas containing a large proportion of CO_2 is not satisfactory for respiration even if the oxygen content is high, because the carbon dioxide deranges the action of the nerve centers, referred to above.

8. Uses of Carbon Dioxide and Properties upon Which Those Uses Depend. (The reader is to summarize these in Exercises, 14, 15.)

Exercises

14. What properties of solid CO_2 make it useful as a refrigerant?

15. What properties of CO_2 make it useful (*a*) in baking, (*b*) in beverages, (*c*) in fire extinguishers, (*d*) as an aid to respiration, (*e*) in photosynthesis?

9. Carbon Monoxide, CO. This gas is formed in motors and furnaces when a limited supply of oxygen is present or when combustion is incomplete. Carbon monoxide is formed from carbon dioxide and carbon in the interior of a bed of burning coal or coke.

Exercise

16. Write the equation for the reaction just mentioned. What becomes of the CO thus formed in a properly operating stove or furnace? What is the source of the CO_2? Write equations for these two reactions.

10. Physiological Effects of Carbon Monoxide. Carbon monoxide is extremely poisonous (toxic) even when inhaled in small quantities. Its high toxicity is due to the fact that it combines with the hemoglobin of the blood, thus preventing the latter substance from performing its normal function of carrying oxygen to all parts of the body. As carbon monoxide possesses no color or odor, there are no warning signs to indicate its presence. A concentration of 1 part of CO in 800 parts of air may cause death within about 30 minutes. Leaking gas pipes or open gas cocks, leaking furnace smoke pipes, improper firing of coal stoves and furnaces, and exhaust gases from automobiles are common sources of carbon monoxide. An automobile engine running in a closed garage may produce sufficient carbon monoxide in 5 to 10 minutes to render a person unconscious. The doors of a garage should always be opened before the engine of an automobile is started. The automobile should be driven out of the garage as soon as possible so that the poisonous exhaust gases may be diffused into the open air.

In firing a furnace or stove, the drafts should be regulated so that there is always a visible flame above the fuel bed. Carbon monoxide burns with a characteristic blue flame which is especially noticeable with hard coal. The luminous flames accompanying the combustion of soft coal are due to the hot carbon from the decomposition of hydrocarbons.

11. Laboratory Preparation of Carbon Monoxide. Small samples of carbon monoxide may be conveniently prepared by allowing formic acid to drop slowly into a flask containing concentrated sulfuric acid, which acts as a dehydrating agent. The flask should be fitted with a dropping funnel and delivery tube so that the carbon monoxide may be collected in a jar by water displacement. The reaction is as follows:

$$\underset{\text{formic acid}}{HCOOH} + H_2SO_4 \rightarrow CO + \underset{\text{hydrate}}{H_2SO_4 \cdot H_2O}$$

Sodium formate may also be used:

$$HCOONa + H_2SO_4 \rightarrow NaHSO_4 + HCOOH$$
$$HCOOH + H_2SO_4 \rightarrow CO + H_2SO_4 \cdot H_2O$$

12. Carbon and Carbon Monoxide as Reducing Agents in Metallurgy. The oxide of zinc or of any less active metal can be reduced to the free metal by action of C or CO at a sufficiently high temperature. If carbon is used, either CO_2 or CO may be formed, depending chiefly upon the temperature used. These reactions are of great industrial importance since the common metals, iron and zinc, are obtained commercially from their ores by this method

TABLE I

CLASSIFICATION OF FUELS*

Physical state	Natural or primary fuels	Prepared or secondary fuels
Solid	Wood Peat Lignite Coal	Charcoal Briquettes Coke Petroleum coke
Liquid	Crude petroleum	Tar Petroleum distillates Gasoline Kerosene Gas oils Petroleum residues Fuel oils Alcohol Colloidal fuels
Gaseous	Natural gas	Coal gas Producer gas Water gas Mixed water gas Carbureted (enriched) water gas Blast-furnace gas Acetylene

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* LEIGHOU, "Chemistry of Engineering Materials," p. 34, McGraw-Hill Book Company, Inc., New York. 1942.

Exercise

17. Write equations for the reaction of each of the following oxides with C and with CO: (*a*) Fe_2O_3, (*b*) CuO, (*c*) Sb_2O_3, (*d*) HgO, (*e*) ZnO.

13. Fuels. Any substance used to produce heat or power by combustion may be regarded as a fuel.

14. Charcoal and Coke. Charcoal is made by heating wood at a high temperature in the absence of air. Coke is made from bituminous coal by a similar process. In this process, the volatile matter in the wood or coal is driven off by the heat, leaving a solid residue which consists largely of fixed carbon and ash as indicated in Table II.

Table II*

	Water, %	Volatile combustible, %	Fixed carbon, %	Sulfur, %	Ash, %
Coal, bituminous	4.50	25.40	64.25	0.87	5.85
Coke	....	0.73	90.49	0.78	8.78

* Leighou, "Chemistry of Engineering Materials," p. 44 McGraw-Hill Book Company, Inc., New York, 1942.

Previous to 1910, most of the coke was produced in *beehive* coke ovens from which the valuable volatile matter was allowed to escape into the air and was lost. In 1937, about 95 per cent of the coke was produced in by-product coke ovens, in which the volatile matter (gas, tar, and ammonia) is saved and converted into useful products.

15. Producer Gas. Producer gas is made by blowing a mixture of air and steam through coal or coke in a special unit known as a *gas producer*. The reactions that take place in the gas producer are the following:

$$\begin{array}{lll} C + O_2 & \rightarrow CO_2 & \text{(exothermic)} \\ C + CO_2 & \rightarrow 2CO & \text{(endothermic)} \\ C + \underset{\text{steam}}{H_2O} & \rightarrow CO + H_2 & \text{(endothermic)} \end{array}$$

The nitrogen of the air that is retained in the resulting mixture reduces the heating value of producer gas. The chief components are

CO	22 per cent
H_2	10 per cent
N_2	58 per cent
CO_2, etc	10 per cent

16. Water Gas. Water gas is made by passing steam through hot coke or anthracite coal. In the actual operation, air is blown through the hot carbon until the temperature reaches a high point.

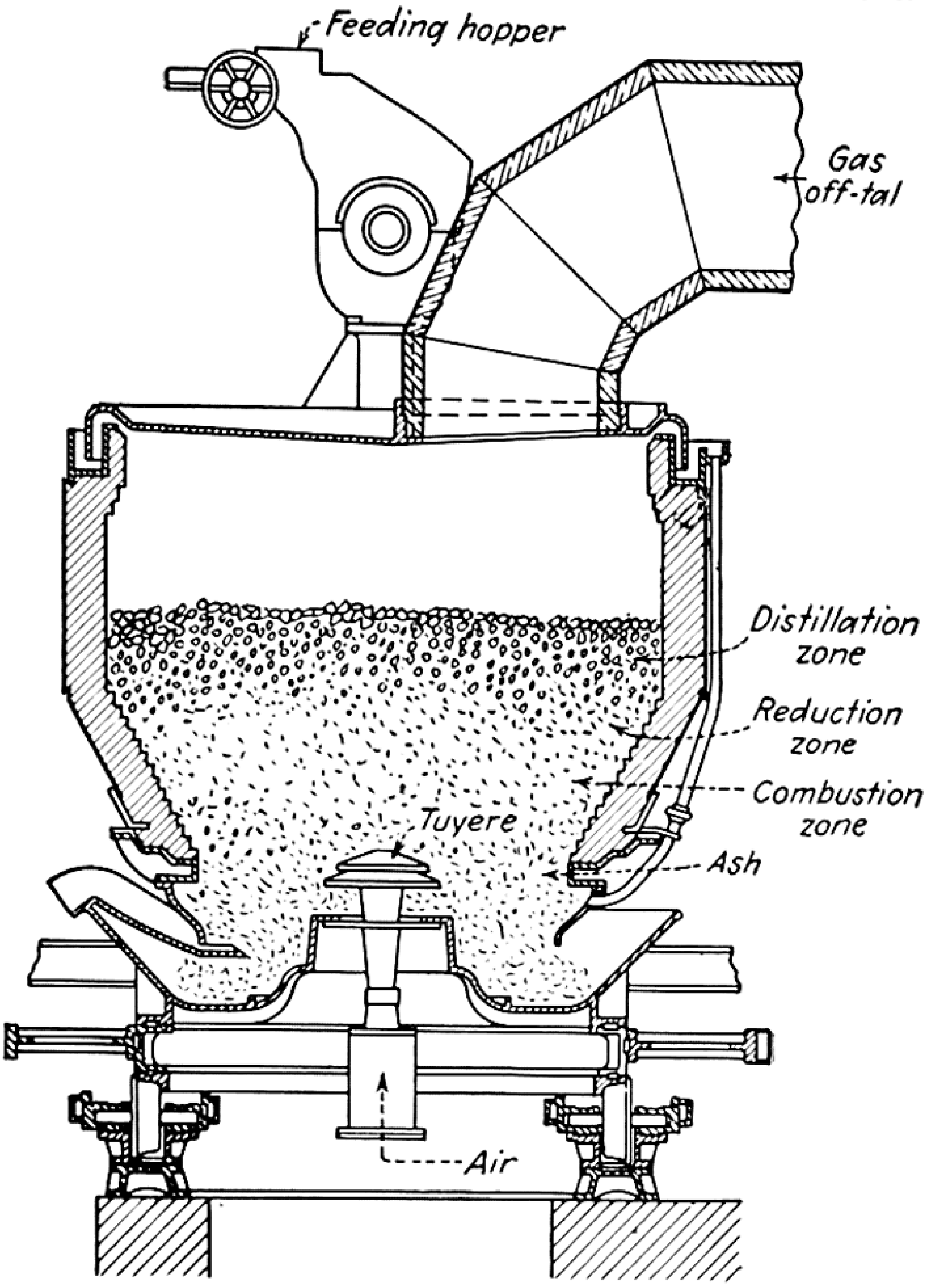

FIG. 2. Cross section of a gas producer. (*Leighou, "Chemistry of Engineering Materials," McGraw-Hill Book Company, Inc.*, 1931.)

The air supply is then cut off and steam is passed through the hot carbon. The reaction of steam with carbon is as follows:

$$H_2O + C \rightleftarrows CO + H_2$$

Since this latter reaction is endothermic, the carbon cools and air must again be admitted. The air and steam treatments are carried on intermittently. Since water gas is composed largely of carbon monoxide and hydrogen, both of which are combustible gases, this fuel has a relatively high heating value. Hydrocarbon compounds are usually added to enrich the gas, *i.e.*, increase the heating value. The product is called *carbureted water gas*.

It is to be noted that, in the manufacture of producer gas, the products of the air and the steam reactions with carbon are all collected in the gas holder. This explains the high percentage (58 per cent) of nitrogen and the low heating value of producer gas. In the manufacture of water gas, only the carbon monoxide and hydrogen are collected in the gas holder, thus accounting for the higher heating value of the water gas.

The heating value of a fuel is expressed in British thermal units. The British thermal unit (B.t.u.) is the quantity of heat required to raise the temperature of 1 lb. of water, 1°F. (usually 39 to 40°F.). Average heating values are as follows:

Producer gas	130 B.t.u. per cubic foot
Water gas	300 B.t.u. per cubic foot

Exercises

18. Calculate the weight of fixed carbon in 1 ton of (*a*) bituminous coal, (*b*) coke (from Table II).

19. It is desired to heat 70 lb. water per hour from 45 to 95°F. What volume of water gas must be burned per hour, assuming that 20 per cent of the heat is lost in various ways?

20. What volume of air (20 per cent O_2) is used to burn completely 1,000 cu. ft. of producer gas containing 20 per cent CO and 10 per cent H_2, the remainder of the gas being noncombustible (Sec. 14)? (Use Avogadro's principle, XIII, 3 and 5.)

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QUINN, Carbon Dioxide and Life, *J. Chem. Education*, **7**, 151 (1930); Carbon Dioxide, Its Industrial Application, *J. Chem. Education*, **7**, 403 (1930); Carbon Dioxide, Its Commercial Manufacture, *J. Chem. Education*, **7**, 637 (1930).

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CHAPTER XXII

HYDROCARBONS, PLASTICS

Gasoline, fuel oils and gases, and lubricating oils are the most important industrial materials composed of carbon and hydrogen (hydrocarbons). A complete study of hydrocarbons would require considerable time. Because of their practical importance, however, it seems desirable to consider briefly this important group of carbon compounds.

1. Definition and Examples. A hydrocarbon is a compound containing only carbon and hydrogen. Natural gas is a mixture of several hydrocarbons. Petroleum is a very complex mixture containing many hydrocarbons, as well as some compounds of oxygen, sulfur, and other elements. Gasoline, kerosene, fuel oil, lubricating oil, vaseline, and paraffin are mixtures of hydrocarbons. Natural rubber, $(C_5H_8)_x$, turpentine, $C_{10}H_{16}$, naphthalene, $C_{10}H_8$, and acetylene, C_2H_2, are hydrocarbons.

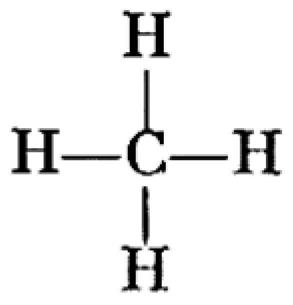
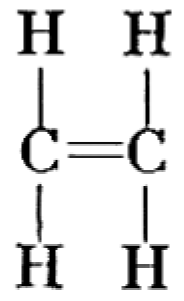
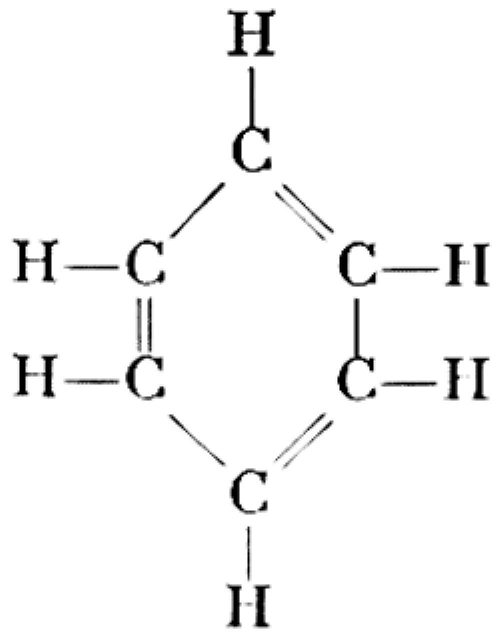
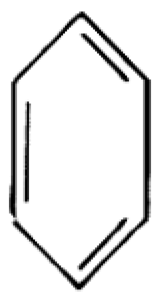
2. Names and Formulas of Typical Hydrocarbons. Thousands of different hydrocarbons are already known, and chemists can synthesize many more if it becomes desirable or interesting to do so. Hydrocarbons are classified into various series. In the left-hand column of Table I, four important series are named. Opposite each are indicated pertinent facts concerning the members of each series. There are many members in each series, but it is important to observe that there are definite relationships for the number of carbon and hydrogen atoms as shown by the *general formulas* for the various series. The general formula, C_nH_{2n+2}, indicates that every member of the paraffin series has two more than twice as many hydrogen atoms as carbon atoms per molecule. (n equals the number of atoms of carbon.)

Exercise

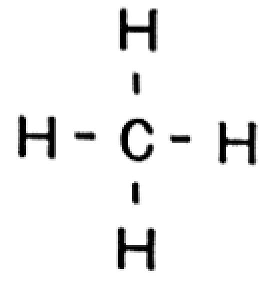
1. Write an empirical formula for the hydrocarbon of each of the four series in Table I that contain (*a*) 7 carbon atoms, (*b*) 10 carbon atoms.

3. Valence of Carbon in Hydrocarbons. Structural Formulas. The valence of carbon is almost uniformly 4. The ordinary schemes for finding valence from formulas do not give this result when applied to the formulas of hydrocarbons because carbon atoms are unusual in that they use some of their valences for combination with other carbon atoms. For instance, in C_2H_2 it would appear that C has a valence of 1. Actually the valence of C is 4, because 3 of the 4 valences of each carbon atom are used for combination with the other carbon atom. This makes use of 6 of the 8 valences possessed by the 2 carbon atoms, leaving 2 valences for combination with other elements.

TABLE I
SOME COMMON HYDROCARBONS

Names of series	Names and formulas of typical members	Structural formulas	Types of bonds	Properties
Methane or paraffin series	Methane, CH_4 Ethane, C_2H_6 Propane, C_3H_8 General formula, C_nH_{2n+2}	 $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$	All single bonds	Saturated. Inert at ordinary temperature
Ethylene or olefin series	Ethylene, C_2H_4 Propylene, C_3H_6 General formula, C_nH_{2n}	 $\mathrm{\overset{\displaystyle H}{\underset{\displaystyle H}{C}}=\overset{\displaystyle H}{\underset{\displaystyle H}{C}}}$	One double bond	Unsaturated. Combine with H_2, Cl_2, Br_2, etc.
Acetylene series	Acetylene, C_2H_2 General formula, C_nH_{2n-2}	$H-C\equiv C-H$	One triple bond	Unsaturated
Benzene or aromatic series	Benzene, C_6H_6 Toluene, C_7H_8 Xylene, C_8H_{10} General formula, C_nH_{2n-6}		Three double bonds in benzene ring 	Unsaturated

The valence relationships in hydrocarbons and other carbon compounds are indicated by means of *structural* or *graphic formulas*. Thus, the structural formula for CH_4 is written:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

This type of formula shows not only the number and kind of atoms in the molecule but also how these atoms are combined and arranged. Structural formulas for other hydrocarbons are given in Table I. The lines joining atoms are called *valence bonds*. The valence of an atom must be the same as the number of its valence bonds. Note in Table I that every C atom has four bonds, every H atom only one bond. It is particularly to be observed that each series of hydrocarbons has structural formulas with a distinct characteristic, such as absence of double or triple bonds in the methane series, presence of a double bond in the olefin series, etc.

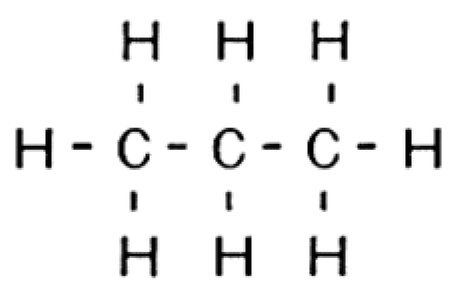
The valence bonds so commonly used in organic chemistry are empirical forms for representing the relationships of the carbon and hydrogen atoms in the hydrocarbon molecule. We know that carbon has 4 valence electrons and that hydrogen has 1 valence electron. The structural formulas shown in the preceding sections may be explained by considering the possible arrangements of the electrons in the molecules of the various hydrocarbons. A detailed study of this field is beyond the scope of this book.

4. Saturated and Unsaturated Hydrocarbons. All the members of the olefin (C_nH_{2n}) series are referred to as *unsaturated* hydrocarbons because they will readily undergo direct addition with many other substances, particularly the elements H_2, Cl_2, and Br_2. For instance,

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2 \qquad \text{(ethylene dibromide)}$$
$$C_3H_6 + H_2 \rightarrow C_3H_8$$

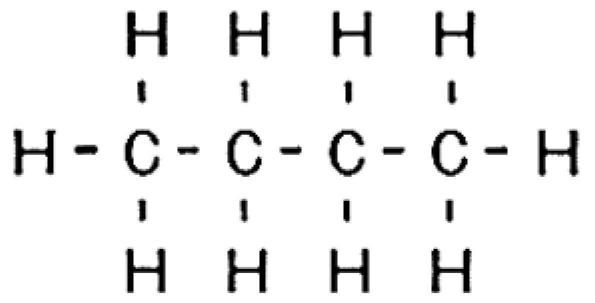
The acetylene and benzene series of hydrocarbons are also referred to as unsaturated hydrocarbons. Hydrocarbons of the methane series are referred to as *saturated*, because they fail to undergo the above type of reaction. They are almost entirely inert at room temperature.

5. Isomers and Isomerism. The structural formula for the hydrocarbon, propane, C_3H_8, is easily represented as



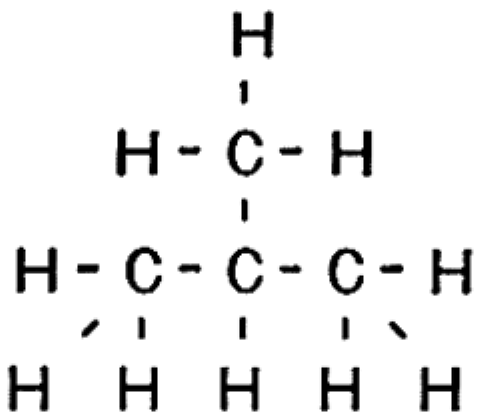
$$\begin{array}{ccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

but when one attempts to write the formula for butane, C_4H_{10}, an interesting problem is involved. Two entirely different ways of arranging the atoms are possible:



normal butane

and



isobutane

Which of the above formulas is the correct one? The answer is that both formulas are correct since two different hydrocarbons having the formula, C_4H_{10}, are known. These are known as *isomers*. The phenomenon of structural isomerism is very common and, in the many cases investigated, the number of isomers actually known corresponds exactly with the number of structural formulas possible.

6. Uses of Important Hydrocarbons. Methane, ethylene, acetylene, and benzene are all produced and used on a large scale. Their sources and uses are indicated in Table II.

TABLE II
SOURCES AND USES OF HYDROCARBONS

Hydrocarbon	Sources	Uses
Methane	Laboratory—soda lime and sodium acetate Industrial—natural gas	Fuel Source of carbon black
Ethylene	Cracking of petroleum products Decomposition of ethyl alcohol by a catalyst (Al_2O_3)	Ripens fruits Source of ethyl alcohol, ethylene glycol or Prestone, antifreeze, and other chemicals
Acetylene	Calcium carbide and water	Oxyacetylene torch Manufacture of rayon, etc.
Benzene	Coal tar	Dyes and drugs

Exercises

2. Write equations for the following reactions:

(*a*) Sodium acetate, CH_3COONa, with soda lime ($NaOH$, and $Ca(OH)_2$). (Use only $NaOH$.) (CH_4 and Na_2CO_3 are formed.)

(*b*) Calcium carbide, CaC_2, with water. [C_2H_2 and $Ca(OH)_2$ are formed.]

3. Show how to calculate the volume of acetylene gas measured at 22°C. and 748 mm., produced by the reaction of 100 g. calcium carbide with water.

7. Combustion of Hydrocarbons. Combustion is their outstanding chemical property. With sufficient oxygen or air and proper mixing, all hydrocarbons burn with evolution of heat to form CO_2 and H_2O. This is called *complete combustion.* For example,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

With an insufficient amount of oxygen, CO and H_2O, C and H_2O, and other products may be formed. This is called *incomplete combustion.* For example,

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

It is possible to calculate the volume of oxygen and of air used and the volume of residual carbon dioxide and nitrogen in the flue gases in the combustion of complex mixtures of gases, *e.g.*, carbureted water gas. The combustion equations are written and the relative volumes of gases involved are calculated by the use of Avogadro's principle (XIII, 3 and 5). The following example is solved as an illustration, the careful study of which will enable the student to work out other similar examples (Exercise 4).

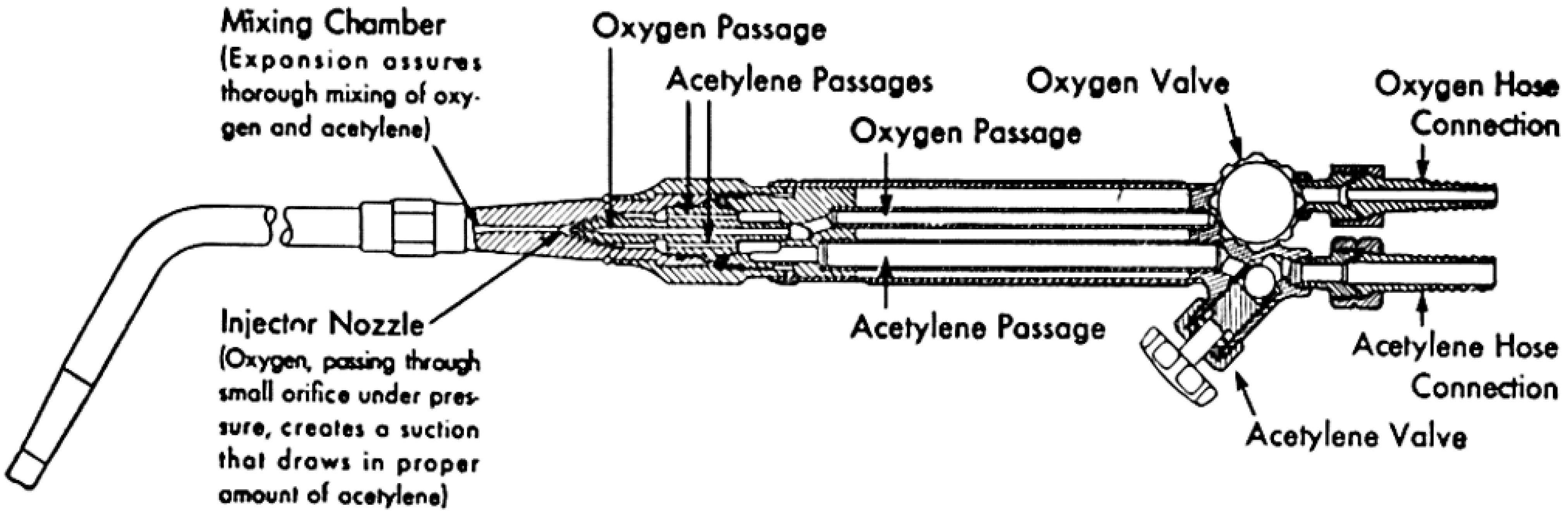

Mixing Chamber (Expansion assures thorough mixing of oxygen and acetylene)
Oxygen Passage
Acetylene Passages
Oxygen Valve
Oxygen Hose Connection
Oxygen Passage
Injector Nozzle (Oxygen, passing through small orifice under pressure, creates a suction that draws in proper amount of acetylene)
Acetylene Passage
Acetylene Hose Connection
Acetylene Valve

FIG. 1. Oxyacetylene welding torch (cross section). (*The Linde Air Products Company.*)

Example. A carbureted water gas has the following composition: 14 per cent CH_4; 12 per cent C_2H_4; 34 per cent CO; 2 per cent CO_2; 36 per cent H_2; 2 per cent N_2.

Calculate (*a*) the total volume of oxygen required to burn completely 100 cu. ft. of this gas, (*b*) the total volume of air required, (*c*) the total volume of carbon dioxide formed by the combustion, (*d*) the total volume of residual carbon dioxide in the flue gases, (*e*) the total volume of residual nitrogen in the flue gases. (Assume that air contains 20 per cent O_2 and 80 per cent N_2 and that all gases are at the same temperature and pressure.)

Solution: From the percentage composition, it follows that 100 cu. ft. of the fuel gas contain the equivalent of the following pure combustible gases:

14 cu. ft.	CH_4
12 cu. ft.	C_2H_4
34 cu. ft.	CO
36 cu. ft.	H_2

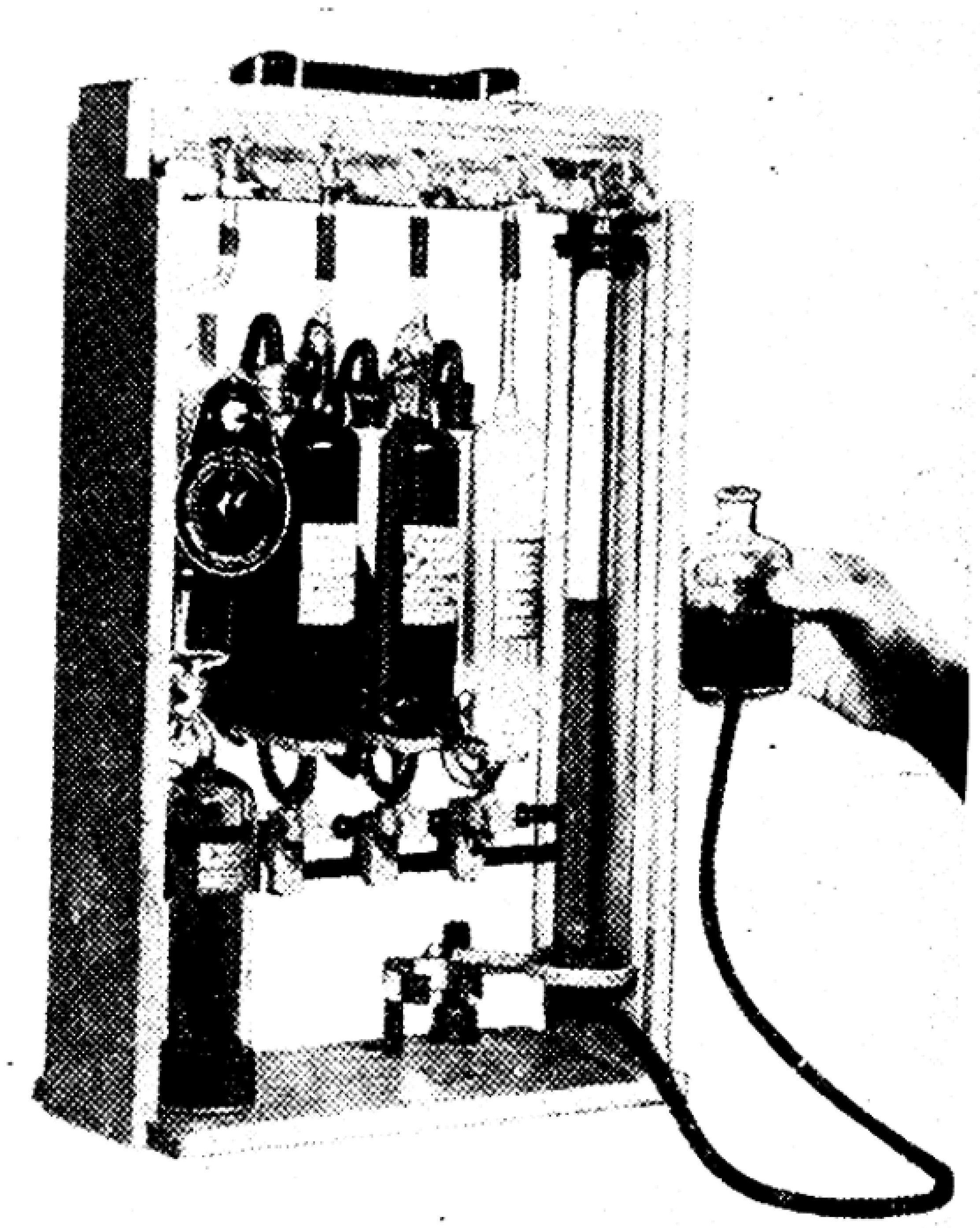


FIG. 2. Apparatus for gas analysis. (*Burrell Technical Supply Company.*)

For the combustion reactions, we have the following equations:

$$\begin{array}{ccccccc} CH_4 & + & 2O_2 & \rightarrow & CO_2 & + & 2H_2O \\ \text{1 mole} & & \text{2 moles} & & \text{1 mole} & & \\ \text{1 vol.} & & \text{2 vol.} & & \text{1 vol.} & & \\ \text{14 cu. ft.} & & \text{28 cu. ft.} & & \text{14 cu. ft.} & & \end{array}$$

$$\begin{array}{ccccccc} C_2H_4 & + & 3O_2 & \rightarrow & 2CO_2 & + & 2H_2O \\ \text{12 cu. ft.} & & \text{36 cu. ft.} & & \text{24 cu. ft.} & & \end{array}$$

$$\begin{array}{ccccc} 2CO & + & O_2 & \rightarrow & 2CO_2 \\ \text{34 cu. ft.} & & \text{17 cu. ft.} & & \text{34 cu. ft.} \end{array}$$

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \rightarrow & 2H_2O \\ \text{36 cu. ft.} & & \text{18 cu. ft.} & & \end{array}$$

a. Total volume O_2 required, $28 + 36 + 17 + 18 = 99$ cu. ft. O_2.

b. Total volume air required, 99 cu. ft. $O_2 \times \frac{100}{20} = 495$ cu. ft. air.

c. Total volume CO_2 formed, $14 + 24 + 34 = 72$ cu. ft. CO_2.

d. Total volume residual CO_2 in flue gases, $14 + 24 + 34 + 2 = 74$ cu. ft. CO_2. (The 2 cu. ft. of CO_2 was in the original gas.)

e. Total volume residual N_2 in flue gases, ($\frac{80}{100} \times$ total volume air used) + (2 cu. ft. N_2 in the original gas) = ($\frac{80}{100} \times 495$) + 2 cu. ft. = 398 cu. ft. N_2.

Exercise

4. A sample of natural gas has the following composition: 84 per cent CH_4; 12 per cent C_3H_8; 4 per cent N_2.

For the combustion of 100 cu. ft. of this gas, calculate (*a*) the total volume of oxygen required, (*b*) the total volume of air required, (*c*) the total volume of carbon dioxide formed, (*d*) the total volume of residual nitrogen in the flue gases. (*e*) Compare the total volume of gas plus air admitted to the burner, with the total volume of carbon dioxide, nitrogen, and steam in the flue gases. Explain the reason for the difference in these total volumes. (Note the relative volumes in the combustion equations.) Assume that all gases are at the same pressure and temperature and that the latter is above the boiling point of water.

8. Cracking of hydrocarbons is another important property. Heat in the absence of air or oxygen causes hydrocarbons to undergo cracking or decomposition. For example,

$$C_{12}H_{26} \rightarrow C_5H_{12} + C_7H_{14}$$

or other products, depending upon operating conditions.

Such cracking usually involves the decomposition of a large molecule into several smaller molecules. It is of great importance in converting kerosene and heavier petroleum fractions into gasoline.

9. The destructive distillation of coal produces large supplies of aromatic and other hydrocarbons as well as other products, as summarized below.

Bituminous coal heated in absence of air
- Ammonia
- Coal gas—Benzene and toluene are "scrubbed" out of gas. Contains CH_4 and H_2 as main components (after purification)
- Coal tar—Yields phenol and many other compounds. Source of dyes
- Coke —Used as a fuel

10. Petroleum Refining. The first step in the refining of petroleum is *fractional distillation*. By this means the petroleum is divided into a number of *fractions* depending upon the boiling points. The more important of these products are shown in Table III.

Petroleum is such a complicated mixture that the fractional distillation process makes no attempt to separate individual hydrocarbons. Each of the above fractions contains many hydrocarbons, but all the hydrocarbons in any one fraction have definite ranges in the boiling point.

11. Motor Fuels. The demand for gasoline is so great that it is common practice to use a large portion of fractions C_{10} to C_{20} (Sec.

10) in the cracking process. Cracking involves heating certain hydrocarbons at a high temperature and at a suitable pressure, producing hydrocarbons of lower molecular weight. Processes have been developed recently for making *polymer gasoline* from the gas. The gasoline produced by cracking and by the polymer process is generally superior to that produced by fractional distillation. Modern motor fuel is a mixture of the above types of gasoline.

TABLE III
SOME PETROLEUM PRODUCTS

Fraction	Approximate number of carbon atoms	Uses
1. Gas	C_1 to C_4, *e.g.*, CH_4 to C_4H_{10}	Fuel Synthetic rubber
2. Gasoline	C_5 to C_{10}	Motor fuel
3. Kerosene	C_{10} to C_{15}	Tractor fuel Heating Illumination
4. Fuel oil	C_{15} to C_{20}	Diesel fuel Heating
5. Lubricating oil	C_{20}, etc.	Lubrication
6. Heavy oil	C_{20} to C_{35}, etc.	Fractionated to Vaseline, tar, Tarvia, etc. Asphalt Coke

12. Octane Number. For satisfactory performance, motor fuels must meet many tests, one of them being *knock rating* or *octane number.* This is measured by means of standard mixtures composed of two pure hydrocarbons called *normal heptane*, C_7H_{16}, and *isooctane*, C_8H_{18}. Normal heptane was chosen because it knocked worse than any other substance tried at the time. If a gasoline knocks as badly as normal heptane, it is given a zero octane number. Isooctane, on the other hand, knocks only under the most adverse conditions. A gasoline that knocks as little as isooctane is given an octane number of 100. A gasoline that knocks the same as a 50-50 mixture of octane and heptane is given an octane number of 50. Most motor fuels have an octane number of about 70; *i.e.*, they knock the same as the mixture containing 70 per cent octane and 30 per cent heptane. Modern aviation fuel specifications often call for a knock rating of 100 or more. In fact isooctane is now made commercially for aviation fuel, and fuels of high octane number were used in very large quantity in military aviation. These highly efficient fuels are of special importance in aviation because they make it possible to cut down the gasoline required, and thus to increase the pay load, especially on long trips.

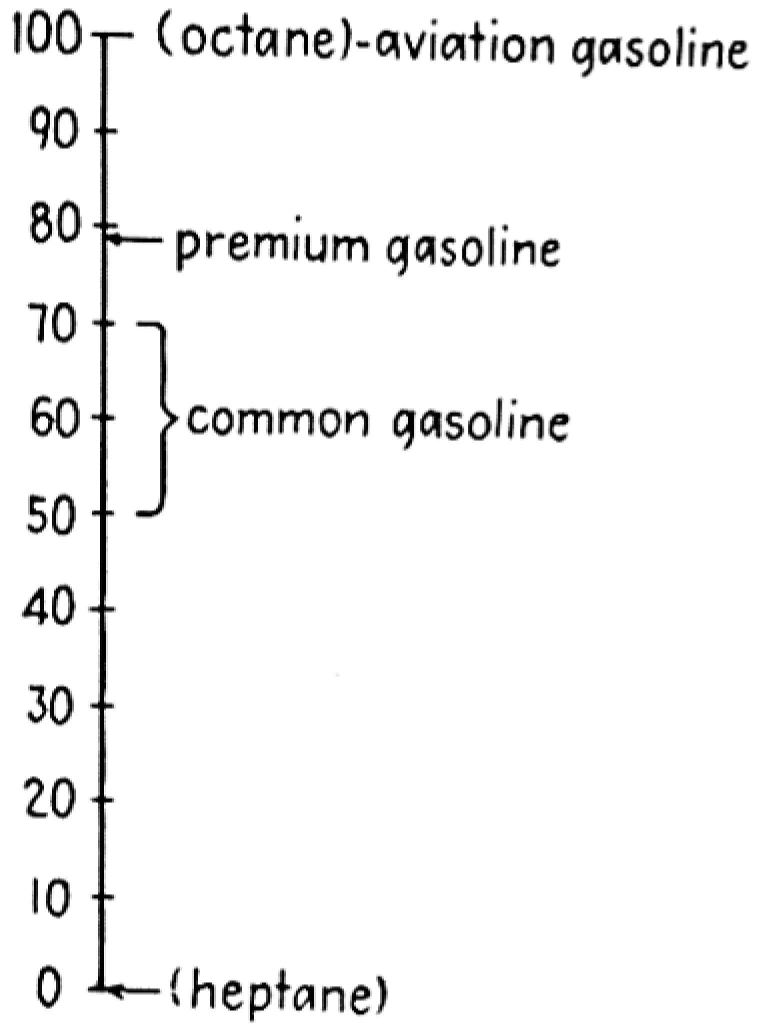


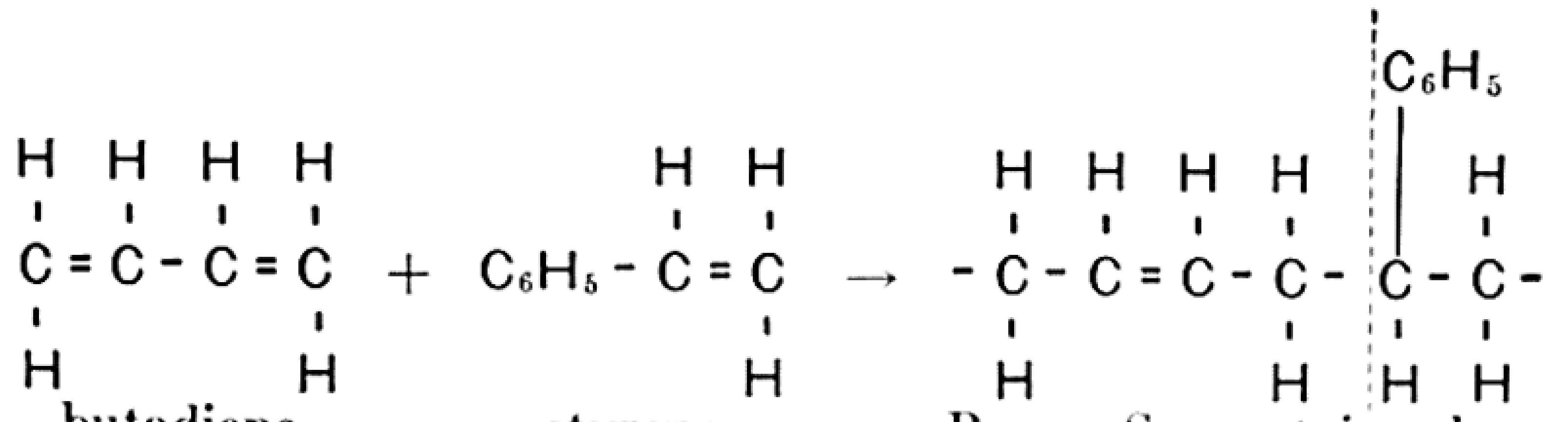
FIG. 3. Octane number of gasoline.

PLASTICS

13. Polymerization, Synthetic Rubber, Plastics. Polymerization is essentially the formation of large molecules by the combination of smaller molecules. The process may be illustrated by the simple case of the formation of benzene from acetylene:

$$3C_2H_2 \rightarrow C_6H_6$$

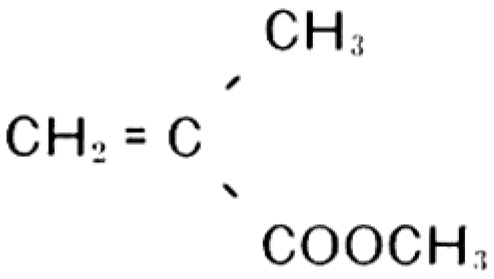
From the beginning of the Second World War, the need for synthetic rubber was very urgent. One of the most common of the synthetic rubbers is Buna S. The name is derived from the materials used in the manufacture of this product, *viz.*, butadiene, $CH_2CHCHCH_2$, or C_4H_6, styrene, $C_6H_5CHCH_2$, and a catalyst (sodium or some other material). The formation of a unit polymer molecule may be regarded as follows:



$$\begin{array}{ccccccc} H & & H & & H & & H \\ | & & | & & | & & | \\ C & = & C & - & C & = & C \\ | & & & & & & | \\ H & & & & & & H \end{array} + \begin{array}{ccccc} & & H & & H \\ & & | & & | \\ C_6H_5 & - & C & = & C \\ & & & & | \\ & & & & H \end{array} \rightarrow \begin{array}{ccccccccccccc} & & & & & & & & & C_6H_5 & & & \\ & H & & H & & H & & H & & | & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C & = & C & - & C & - & C & - & C & - \\ & | & & & & & & | & & | & & | & \\ & H & & & & & & H & & H & & H & \end{array}$$

butadiene — styrene — Buna S contains large numbers of these polymer units

Another product known as *lucite* or *plexiglas* is made by the polymerization of the substance, methyl methacrylate,



$$CH_2 = C \begin{array}{l} \diagup CH_3 \\ \diagdown COOCH_3 \end{array}$$

The molecules join each other at the double bonds. This material is widely used as the transparent covering for the nose or "greenhouse" of airplanes.

The so-called *vinyl resins* are made by the polymerization of vinyl chloride, $CH_2{=}CHCl$. Polymers of indefinite molecular size, *e.g.*, $—CH_2—CHCl—CH_2—CHCl—$, may be formed. This type is known as a *linear polymer.*

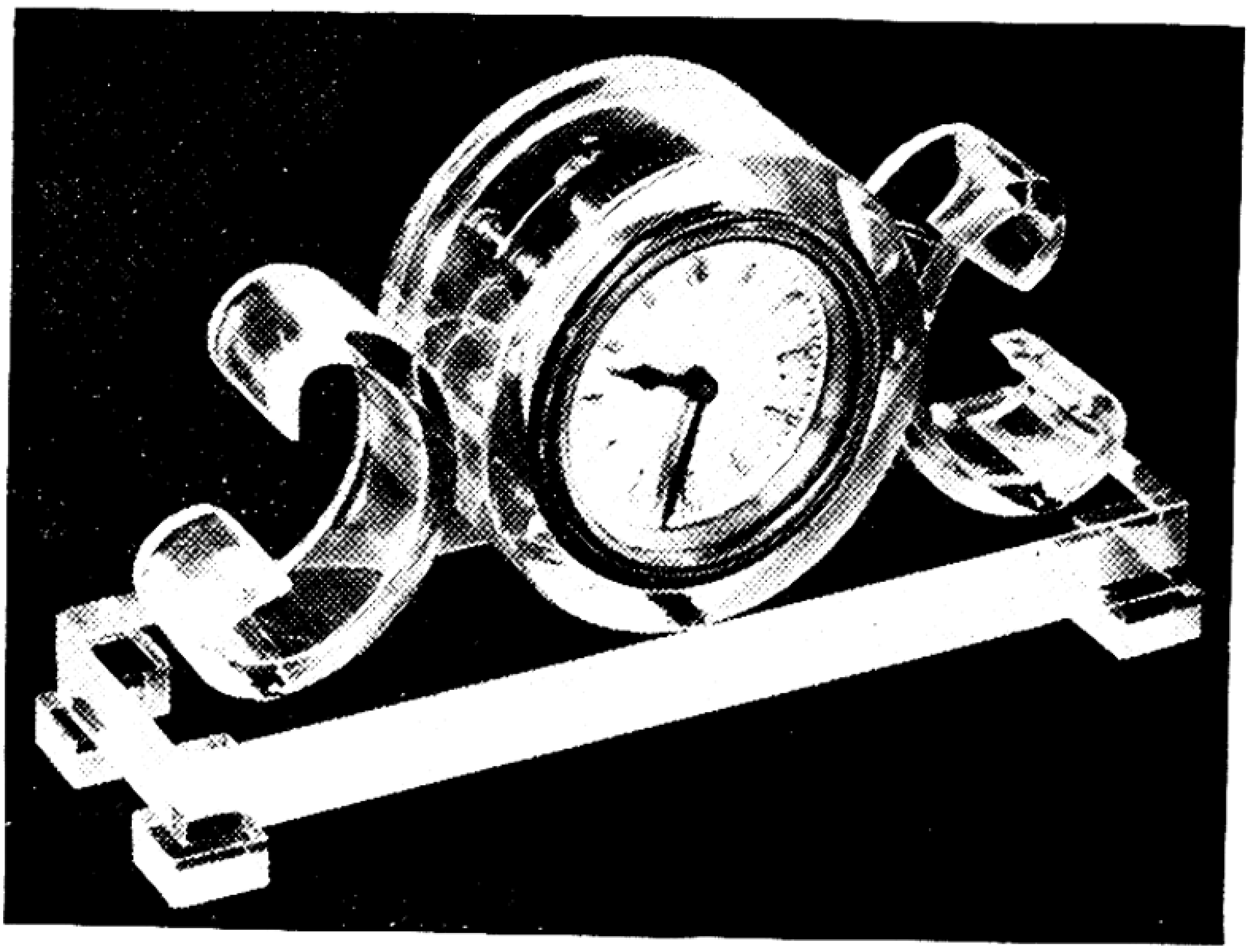


FIG. 4. Plexiglas clock frame. (*Rohm and Haas Company.*)

Bakelite is an older plastic familiar in electric switches, radio dials, etc. It is made from phenol, C_6H_5OH, and formaldehyde, HCHO, and is named after Dr. Leo Baekeland who developed the synthesis and founded the corporation that manufactures this product.

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CHAPTER XXIII

CARBOHYDRATES AND FOODS

Hydrocarbons and carbohydrates are very important carbon compounds. Organic chemistry is the study of compounds of carbon. More than 300,000 such compounds are known. Before 1828 it was thought that they could be formed only by natural processes. Since that time, thousands of organic compounds have been synthesized in the laboratory. Among these are many dyes and drugs, and more recently, vitamins and hormones. We shall now study, briefly, certain organic compounds found in foods, plants, and related materials.

1. **Carbohydrates** are compounds of carbon, hydrogen, and oxygen with the latter two elements usually in the same proportions as in water. Cellulose, starch, and sugar are common carbohydrates.

2. **Photosynthesis.** Cellulose is formed by the process of photosynthesis in growing plants. This may be represented in a simplified form by the equation

$$6CO_2 + 5H_2O \rightarrow \underset{\text{cellulose}}{(C_6H_{10}O_5)_y} + 6O_2 - \Delta$$

The process of photosynthesis is actually much more complicated since it apparently takes place in a series of steps in which simpler compounds are converted first into sugar and then to starch or cellulose. It is an endothermic reaction, as indicated by the heat term ($-\Delta$) in the above equation. The reaction occurs only in the presence of sunlight and chlorophyll.

The process of photosynthesis is essentially the reverse of combustion or oxidation. These processes are continually taking place; hence the carbon dioxide and oxygen content of the atmosphere can vary but slightly even over a long period of time. Photosynthesis is especially significant because at present it is the only chemical process by means of which energy from outside the earth is collected and stored.

3. **Cellulose** is a white solid whose formula is usually represented as $C_{6y}H_{10y}O_{5y}$ or $(C_6H_{10}O_5)_y$. The total number of atoms in the cellulose molecule is unknown and probably varies in an indefinite manner. Wood and cotton are the chief commercial sources of cellulose. Filter

paper is nearly pure cellulose. Ordinary paper is chiefly cellulose, but it also contains added materials to confer the desired properties (body, weight, gloss, absence of pores, etc.).

The chief chemical properties of cellulose are combustibility, its reactions with nitric acid to form cellulose nitrate, and some similar reactions with other acids.

4. Manufacture of Paper. Paper is a thin mat of interwoven cellulose fibers. Although the better grades of paper are made from linen or cotton, wood is the chief raw material for making the common newspaper stock. Bamboo, cornstalks, or straw may also be used. The various steps involved in the manufacture of paper are essentially the following:

a. Chipping or grinding the wood. This is purely a mechanical process which reduces the wood to small particles that can be readily treated.

b. Cooking with calcium bisulfite, $Ca(HSO_3)_2$, which disintegrates the chips and removes the gummy binding material (lignin) in the natural wood. This process requires large quantities of sulfur for making the bisulfite and is known as the *sulfite process.*

c. Beating and washing with steam and mechanical agitation aid in the further disintegration of the pulp.

d. Bleaching with hypochlorite solution to destroy the natural coloring material in the wood.

e. Rolling and drying. This treatment is also a mechanical process which requires a long series of sieves and rollers.

f. Tinting, sizing, or glazing processes are also required for special writing papers upon which ink is to be used.

5. Starch has the same composition as cellulose. Its formula is $C_{6x}H_{10x}O_{5x}$ or $(C_6H_{10}O_5)_x$. The value of x is smaller in this case than the y used in the cellulose formula but is otherwise unknown.

Exercises

1. Name two sources of starch.
2. State the reagent used, and the color produced in the test for starch (refer to textbooks in biology; also XI. 2).

Starch does not dissolve in water, but upon heating it is finely dispersed to form a colloidal suspension that is often entirely clear to the naked eye. Upon boiling in the presence of acid, starch undergoes hydrolysis, forming glucose. The H^+ ion of the acid functions as a catalyst.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_x} + xH_2O \xrightarrow{H^+} \underset{\text{glucose}}{xC_6H_{12}O_6}$$

A similar reaction takes place when starch is mixed with saliva because the latter contains the enzyme, *ptyalin*. Ptyalin catalyzes the hydrolysis of starch to maltose.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_x} + xH_2O \xrightarrow{\text{ptyalin}} \underset{\text{maltose}}{xC_{12}H_{22}O_{11}}$$

Yeast contains the enzyme *diastase* which catalyzes the hydrolysis of starch in a manner similar to the reaction with H^+ ion. This is the first step in the production of alcohol from starch.

6. Sugars are carbohydrates having the formulas $C_6H_{12}O_6$ or $C_{12}H_{22}O_{11}$. The former are called *monosaccharides*, the latter *disaccharides*. Glucose and fructose are common monosaccharides; *maltose*, *lactose*, and *sucrose* (ordinary sugar) are disaccharides. Certain sugars (*e.g.*, glucose and maltose) are called *reducing sugars* because they react with cupric ion solutions (Fehling's solution, Benedict's solution XXVI. 10), reducing the valence of copper ion from +2 to +1 and precipitating yellow, orange, or red cuprous oxide, Cu_2O.

7. Hydrolysis or Inversion of Disaccharides. When sucrose solution is boiled with H^+ ion present, the sucrose is converted to glucose and fructose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The H^+ ion functions as a catalyst. In a polariscope, sucrose rotates the plane of polarized light to the right while the glucose-fructose mixture causes rotation to the left. The hydrolysis is therefore called *inversion*, and the glucose-fructose mixture is called *invert sugar*. Inversion is also catalyzed by the enzyme *invertase*.

8. Alcohols. Although there are many alcohols known to the organic chemist, only the two most common ones, ethyl and methyl alcohols, are now to be considered. *Ethyl alcohol* or grain alcohol (ethanol), C_2H_5OH, is made commercially by the fermentation of molasses and other sugar or starch containing mixtures. The reaction is as follows:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Ethyl alcohol is widely used as a raw material in the manufacture of butadiene rubber, as an industrial solvent, and as an ingredient in automobile antifreeze preparations. It is the substance responsible for the intoxicating effects of alcoholic beverages. *Methyl alcohol* (methanol) or wood alcohol, CH_3OH, is made commercially by the destructive distillation of wood and by direct synthesis from carbon monoxide and hydrogen. High temperature, high pressure, and a catalyst are utilized in the latter process. The equation for the reaction is as follows:

$$CO + 2H_2 \xrightleftharpoons[\text{catalyst}]{} CH_3OH$$

Exercises

3. What industrial fuel gas can be used to furnish the carbon monoxide and hydrogen required in the synthesis of methyl alcohol?

4. Show by LeChâtelier's principle why high pressure increases the yield of methyl alcohol.

5. What volume of hydrogen is required to react with 100 cu. ft. of carbon monoxide? What law is illustrated here?

Denatured alcohol is a term applied to commercial ethyl alcohol that is diluted with methyl alcohol, and/or other substances. Since methyl alcohol is poisonous and has very harmful physiological effects (blindness), denatured alcohol cannot be used for beverage purposes. The presence of methyl alcohol, however, does not ordinarily interfere with the technical use of denatured alcohol as a solvent, as an antifreezing preparation, etc.

9. Organic Acids. Acetic acid is probably the most common organic acid. Vinegar contains about 4 per cent of this acid. The formula is written in several different ways, *e.g.*, $HC_2H_3O_2$; $C_2H_4O_2$; HAc; Ac; CH_3COOH. The last formula is, perhaps, the preferable one since it conforms to the general type formula for all organic acids, *viz.*, $R{\cdot}COOH$, in which R represents a hydrocarbon radical. Organic acids of high molecular weight are palmitic acid, $C_{15}H_{31}COOH$; oleic acid, $C_{17}H_{33}COOH$; and stearic acid, $C_{17}H_{35}COOH$.

Acetic acid is made by the oxidation of ethyl alcohol, also from acetylene. The oxidation is carried on by passing the alcohol or fermented fruit juice, *e.g.*, cider, over wood shavings, upon which a material (mother of vinegar) containing certain enzymes, is adsorbed. Air, of course, supplies the oxygen. The equation for the reaction is as follows:

$$C_2H_5OH + O_2 \xrightarrow{\text{enzyme}} CH_3COOH + H_2O$$

Acetic acid is a weak acid, the apparent fraction of ionization being 0.013 or 1.3 per cent in 0.1N solution. The ionization may be expressed by the equation:

$$\mathrm{CH_3COOH} \rightleftarrows \mathrm{CH_3COO^-} + \mathrm{H^+}$$

Note that the hydrogen of the COOH or carboxyl group is dissociated from the molecule.

Exercise

6. Calculate the weight of 4 per cent acetic acid that could be made by the fermentation of 10 lb. glucose and the subsequent oxidation of the alcohol to acetic acid.

10. Fats and Soaps. Common laundry soap is made by heating a mixture of fat and alkali. In order to understand the chemistry of soapmaking, it is desirable to know something about the composition of fats. When an organic acid and an alcohol react, two products are formed: an *ester* and water. For example,

$$\underset{\text{acetic acid}}{\overset{\text{acid}}{\mathrm{CH_3COOH}}} + \underset{\text{ethyl alcohol}}{\overset{\text{alcohol}}{\mathrm{C_2H_5OH}}} \rightarrow \underset{\text{ethyl acetate}}{\overset{\text{ester}}{\mathrm{CH_3COOC_2H_5}}} + \overset{\text{water}}{\mathrm{H_2O}}$$

$$\underset{\text{stearic acid}}{\mathrm{3C_{17}H_{35}COOH}} + \underset{\text{glycerin}}{\mathrm{C_3H_5(OH)_3}} \rightarrow \underset{\text{glyceryl stearate}}{\mathrm{(C_{17}H_{35}COO)_3C_3H_5}} + \mathrm{3H_2O}$$

The ester, glyceryl stearate, or *stearin*, is one of several esters found in animal fats. A fat is an ester of a higher molecular weight acid with glycerin.

Saponification is the reaction by which soap is formed from fat and alkali. It may be illustrated by the following equation:

$$\underset{\text{glyceryl stearate}}{\mathrm{(C_{17}H_{35}COO)_3C_3H_5}} + \mathrm{3NaOH} \rightarrow \underset{\substack{\text{sodium stearate,}\\ \text{soap}}}{\mathrm{3C_{17}H_{35}COONa}} + \underset{\text{glycerin}}{\mathrm{C_3H_5(OH)_3}}$$

If potassium hydroxide is substituted for sodium hydroxide, a liquid or soft soap is formed.

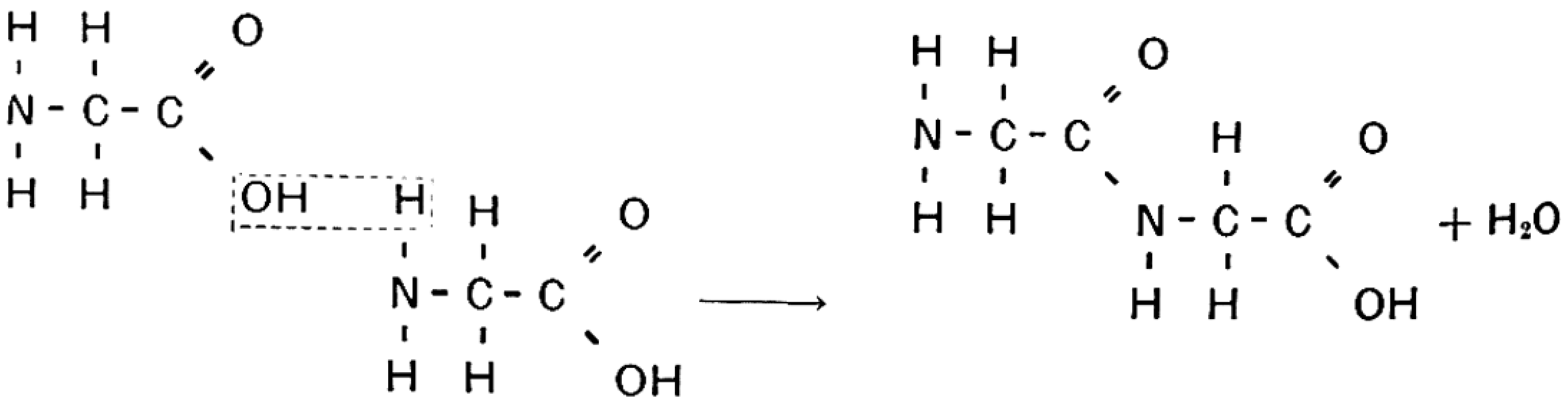
Exercise

7. Calculate (*a*) the weight of sodium hydroxide required to react with 10 lb. glyceryl stearate and (*b*) the weight of sodium stearate soap formed.

The cleansing action of soap depends upon certain properties known as *adsorption* and *emulsification*. Fine particles of dirt are surrounded and removed by the soap solution. Oily matter is reduced to fine droplets which can be easily rinsed off from clothing. For a more complete explanation, the student is referred to books on colloid chemistry.

11. Proteins are complex compounds of carbon, hydrogen, oxygen, and nitrogen, with sulfur and phosphorus also often present. Egg albumin is nearly pure protein, while lean meat, beans, and fish contain a high content of protein. Upon being heated strongly, proteins decompose, leaving carbon as a residue. During the first stages of the decomposition of certain proteins, water and hydrogen sulfide are evolved. Heating with NaOH results in evolution of ammonia.

Proteins are formed by the combination of *amino acids*, a simple illustration of the latter being aminoacetic acid or glycine, NH_2CH_2COOH. The combination or *condensation*, as it is called in organic chemistry, of 2 molecules of amino acetic acid is illustrated as follows:



A large number of molecules of amino acids are thus linked together or condensed, forming proteins of high molecular weight. In the digestion of proteins, the reverse process, or hydrolysis, takes place, which breaks down the proteins into simpler amino acids.

12. Foods. Carbohydrates, fats, proteins, minerals, water, and vitamins are the principal components of foods. Carbohydrates and fats furnish heat and energy for the body, while protein and mineral matter build tissue and bone. The *vitamins* present in small amounts in foods have a very important function in helping to maintain bodily health and vigor. Great progress has been made in recent years in the study of the vitamins, as to their occurrence, chemical composition, and properties. Some of them have been identified as chemical compounds; for example, vitamin C is *ascorbic acid.*

The specialized study of foods and nutrition requires a knowledge of organic chemistry and biological chemistry. Experts in nutrition have formulated diets for people of different ages and occupations, taking into account the energy and vitamin requirements of the individual. In general, it may be stated that (1) people doing heavy manual work require a high protein and carbohydrate diet, (2) people living in cold climates require a high fat diet, (3) all people require sufficient vitamin-containing foods to maintain bodily health and vigor, (4) children need considerable mineral matter to meet the requirements of growing bones and teeth.

Table I

Composition of Foods*

Food	Water, %	Protein, %	Fat, %	Minerals, %	Carbohydrates, %
Almonds (dried)	4.7	18.6	54.1	3.0	19.6
Apples (fresh)	84.1	0.3	0.4	0.29	14.9
Asparagus	93.0	2.2	0.2	0.67	3.9
Bacon	20.0	9.1	65.0	4.3	1.1
Bananas	74.8	1.2	0.2	0.84	23.0
Beans (dried)	10.5	22.0	1.5	3.9	62.1
Beef (dried)	47.7	34.3	6.3	11.6	0.0
Bread (white)	35.9	8.5	2.0	1.3	52.3
Butter	15.5	0.6	81.0	2.5	0.4
Cabbage	92.4	1.4	0.2	0.75	5.3
Celery	93.7	1.3	0.2	1.08	3.7
Cheese (cream)	42.7	14.5	39.9	1.9	1.0
Coconut (fresh)	46.9	3.4	34.7	1.0	14.0
Eggs	74.0	12.8	11.5	1.0	0.7
Ham (smoked, lean)	53.5	20.2	20.8	5.5	0.0
Lettuce	94.8	1.2	0.2	0.9	2.9
Milk	87.1	3.4	3.9	0.7	4.9
Oatmeal (cooked)	84.8	2.3	1.2	0.7	11.0
Olive oil	....	....	100.0		
Oranges	87.2	0.9	0.2	0.47	11.2
Peanuts (roasted)	2.6	26.9	44.2	2.7	23.6
Potatoes	77.8	2.0	0.1	1.0	19.1
Raisins	24.0	2.3	0.5	2.0	71.2
Rice	12.3	7.6	0.3	0.4	79.4
Salmon (canned)	67.4	20.6	9.6	2.4	0.0
Spinach	92.7	2.3	0.3	1.53	3.2
Strawberries	90.0	0.8	0.6	0.5	8.1
Wheat flour	12.0	11.2	1.1	0.5	75.2

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* Chatfield and Adams, The Proximate Composition of American Food Materials, *Circular* 549, U. S. Department of Agriculture.

Exercise

8. From Table I, make a list of (*a*) five food materials containing over 20 per cent protein, (*b*) five food materials containing over 10 per cent fat, (*c*) five food materials containing over 50 per cent carbohydrate, (*d*) five food materials containing 3 per cent or more minerals.

Observe that asparagus, cabbage, celery, lettuce, and spinach contain over 90 per cent water; that beef, ham, and salmon contain no carbohydrate; that olive oil contains 100 per cent fat.

SUGGESTED READING

FOSTER, From Atom to Life, *J. Chem. Education*, **3**, 1391 (1926).
BENSON, The Story of Paper, *J. Chem. Education*, **7**, 1739 (1930).

CHAPTER XXIV

SILICON AND BORON. GLASS

Silicon bears some relationship to carbon. Both elements are in Group IV of the periodic system and possess a valence of 4 in their compounds. Carbon is the predominant element in plant and animal materials, as well as in thousands of synthetic organic compounds. Silicon may be regarded as the predominant element in mineral materials. Both silicon and carbon are nonmetals with very high melting points.

Boron is a nonmetal of Group III of the periodic system. Silicon and boron and many of their compounds possess similar properties and, for this reason, are to be considered, in this chapter, as related elements.

1. Occurrence of Silicon in Nature. Silicon never occurs in nature in the free state, but it is the second most plentiful element in the earth's crust, making up an estimated 26 per cent. Nearly all common rocks except limestone are silicon compounds or mixtures of these compounds. Among the more common or useful silicon-bearing rocks are granite, sandstone, basalt, feldspar, clay and asbestos, talc, soapstone, mica, and the zeolites.

2. Silicon. Manufacture, Properties, and Uses. Large amounts of silicon are produced at Niagara Falls, by heating sand, SiO_2, with coke in an electric furnace in which the following reaction occurs:

$$SiO_2 + 2C \rightarrow Si + 2CO$$

Silicon can also be prepared by heating pure SiO_2 with magnesium in finely divided form.

$$SiO_2 + 2Mg \rightarrow Si + 2MgO$$

The magnesium oxide with uncombined magnesium (and magnesium silicide) is removed by the use of hydrochloric acid.

The crystalline form of silicon is needlelike and has a steel blue luster, and the amorphous form is a brown powder. Silicon is an important material in the iron and steel industry. Alloys of iron known as *Duriron*, containing 10 to 15 per cent silicon, are very resistant to the corrosive action of acids. Such alloys are widely used in the manufacture of drain pipes in laboratories, acid pumps, etc. Owing to the hardness and brittleness of these alloys, they cannot be cut and threaded and must be cast into the form to be used. Silicon in iron increases electrical resistance and promotes grain growth. These properties have led to the use of silicon (1 to 5 per cent) in iron for electrical machinery, *e.g.*, in transformer cores to reduce eddy currents (hysteresis).

Ferrosilicon alloy is used in the manufacture of about 90 per cent of the steel produced in the United States. From the melted steel, the ferrosilicon removes the dissolved oxygen that produces flaws in the product.

3. **Silica** is a synonym for silicon dioxide, SiO_2. Ordinary sand is impure silica. In addition to its importance as an ingredient of concrete, silica is an important raw material in the manufacture of glass, in the recovery of iron from its ores, in the manufacture of silicon carbide, and in other metallurgical and chemical processes. Silica is unusual because it occurs in so many different forms in nature. Thus, quartz, opal, agate, flint and sponge, cameo, diatomaceous earth are all essentially SiO_2.

4. **Water Glass.** When variable quantities of sand are fused with sodium carbonate, a water-soluble material of variable composition is formed. The reaction may be indicated by the equation:

$$Na_2CO_3 + xSiO_2 \rightarrow Na_2O{\cdot}xSiO_2 + CO_2$$

Ordinary water glass is a water solution of the silicate having the composition equivalent to 1 mole of Na_2O to 3.22 moles of SiO_2 (or $1Na_2O:3.22SiO_2$) at 4°Baumé.[1] Water glass is used in enormous quantities as an adhesive in making paper boxes, as a builder and adjunct in soaps, and in preserving eggs. It is also used to make silicic acid and silica gel.

5. **Silicic acid** may be formed by the reaction of an acid with sodium silicate solution.

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3 \text{ or } (xH_2O{\cdot}ySiO_2)$$

The silicic acid usually forms a jellylike mass. There is considerable evidence that this jelly is merely a special kind of mixture of SiO_2 and H_2O rather than a compound of these two substances. Attempts to dry the jelly and prepare H_2SiO_3 result only in obtaining SiO_2.

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[1] Baumé is a term used to indicate a scale of densities used in industry.

The silicic acid jelly is used to prepare activated silica or *silica gel*, a white granular solid, which has a highly porous structure with enormous surface area and is, therefore, used as a catalyst base and as an adsorbent for gases and odoriferous vapors.

Many so-called silicic acids are recognized, in the combined form, as complex silicates of metals, in minerals. These acids may be regarded as combinations of water with silica in varying molar proportions, as shown in Table I.

TABLE I

Acid	Formula	Constituent oxides, xH_2O, $ySiO_2$
Metasilicic	H_2SiO_3	$1H_2O$, $1SiO_2$
Orthosilicic	H_4SiO_4	$2H_2O$, $1SiO_2$
Disilicic	$H_2Si_2O_5$	$1H_2O$, $2SiO_2$
	$H_4Si_2O_6$	$2H_2O$, $2SiO_2$
	$H_6Si_2O_7$	$3H_2O$, $2SiO_2$
Trisilicic	$H_2Si_3O_7$	$1H_2O$, $3SiO_2$
	$H_4Si_3O_8$	$2H_2O$, $3SiO_2$
	$H_6Si_3O_9$	$3H_2O$, $3SiO_2$

Exercise

1. Make a list containing the names of the acids in Table I with the mole per cent of water and silica in each acid. For example, metasilicic acid, 50 mole per cent H_2O; 50 mole per cent SiO_2.

From Table I it will be observed that the disilicic acids contain 2 moles of silica, and the trisilicic acids contain 3 moles of silica. Other higher acids may be identified in the acid radicals of mineral silicates (Table II).

6. Silicates. A few of the more common silicates of industrial importance are listed in Table II. It is to be noted that the formulas of the silicates are expressed, also, in terms of their constituent oxides.

In order to understand the composition of these complex compounds, one should observe the similarities and differences in composition as indicated by the constituent oxides in Table II. Chemical analyses of such materials are always reported in terms of the percentages of the constituent oxides. (It is not expected that the formulas are to be memorized.) Note, for example, that asbestos and meerschaum are magnesium silicates, and that feldspar (potash type) and mica are double silicates of aluminum and potassium.

TABLE II

Silicate	Formula	Constituent oxides
Asbestos	$H_4Mg_3Si_2O_9$	$3MgO, 2SiO_2, 2H_2O$
Meerschaum	$H_4Mg_2Si_3O_{10}$	$2MgO, 3SiO_2, 2H_2O$
Clay (kaolin)	$H_4Al_2Si_2O_9$	$Al_2O_3, 2SiO_2, 2H_2O$
Feldspar	$2AlKSi_3O_8$	$Al_2O_3, 6SiO_2, \ldots K_2O$
Mica	$2H_2KAl_3(SiO_4)_3$	$3Al_2O_3, 6SiO_2, 2H_2O, K_2O$
Zeolite	$H_4Na_2Al_2(SiO_3)_6$	$Al_2O_3, 6SiO_2, 2H_2O, Na_2O$
Garnet	$Ca_3Fe_2(SiO_4)_3$	$Fe_2O_3, 3SiO_2, \ldots 3CaO$

Exercises

2. List the names of the materials in Table II which are silicates of (*a*) disilicic acid, (*b*) trisilicic acid.

3. Calculate (*a*) the mole per cent, (*b*) the percentage by weight cf silica in asbestos and in clay.

4. Calculate (*a*) the mole per cent, (*b*) the percentage by weight of potash (K_2O) in feldspar and in mica.

7. Industrial Importance of Silicates. Asbestos and mica are widely used as insulating materials because of their very low thermal and electrical conductivity. Being noncombustible, tough, and pliable, asbestos cloth is used in making asbestos suits for firemen.

Pure china clay (kaolin) is used in the manufacture of crockery, crucibles, and pottery. The clay, mixed with water, is molded into the desired form and then heated to a high temperature in a kiln. Impure clays containing ferric silicates are raw materials in the manufacture of brick, tile, and portland cement (XXVIII. 11). The iron compounds in clay are responsible for the red color of common building brick. Refractory bricks, suitable for lining fire boxes and furnaces, are made from a special sandstone, SiO_2, known as *ganister*.

Exercise

5. Name two physical or chemical properties of clay that are essential in the manufacture of brick and tile.

The zeolite silicates are widely used in water purification because of their property of removing the calcium and magnesium ions in hard water. Garnet, on account of its great hardness, is used to some extent, in the manufacture of special grinding materials known as *abrasives*. Other widely used abrasives are those containing aluminum oxide (fused) or silicon carbide.

8. Silicon carbide, SiC (Carborundum or Crystolon). An extremely hard substance, silicon carbide, is used in machine shops for sharpening tools and smoothing up metal castings, also in the manufacture of whetstones and emery cloth. It was discovered in 1893 by Edward Acheson, in an attempt to produce materials of great hardness. By heating sand and carbon together in a small electric furnace, Acheson prepared a few beautiful dark purple, iridescent crystals, which he found would scratch glass. The same general process is used today in the manufacture of carborundum and crystolon.

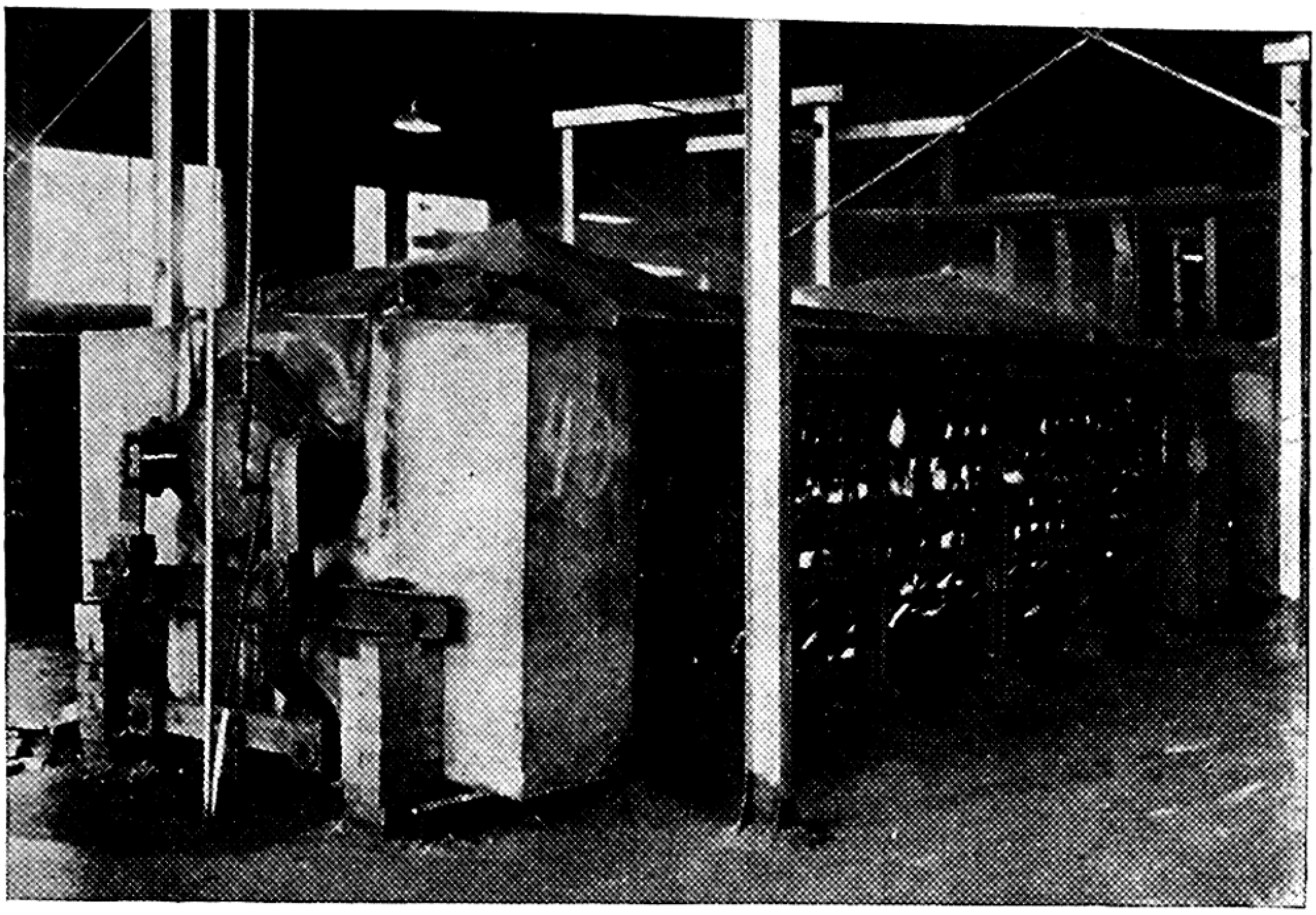

FIG. 1. Fusing sand and coke in resistance-type electric furnace to make silicon carbide (crystolon) abrasive. (*Norton Company.*)

A mixture of sand and coke, with sawdust and salt, is placed in an electric furnace of the resistance type (XXI. 2). A core of graphitized coke, in the center of the mixture, becomes incandescent from the heat generated by the electric current. Within a few hours, large masses of silicon carbide are formed around the core. The product is then crushed, sifted, and mixed into a paste with water glass or other binding materials. The paste, when shaped into grinding wheels, etc., by high pressure, is then fired in a kiln.

By use of the X rays, it has been shown that silicon carbide has a crystal structure resembling that of the diamond. The atoms of silicon and carbon are closely bonded together by shared electrons. With boron carbide, it ranks next to diamond in actual hardness.

9. Boron. The element, boron, is a nonmetal and can be prepared by the reduction of boric oxide, B_2O_3, with magnesium. It exists in two allotropic forms: as an amorphous brown powder and as transparent crystals that resemble the diamond in brilliance and hardness. Boron forms two very important compounds: *borax* and *boric acid.*

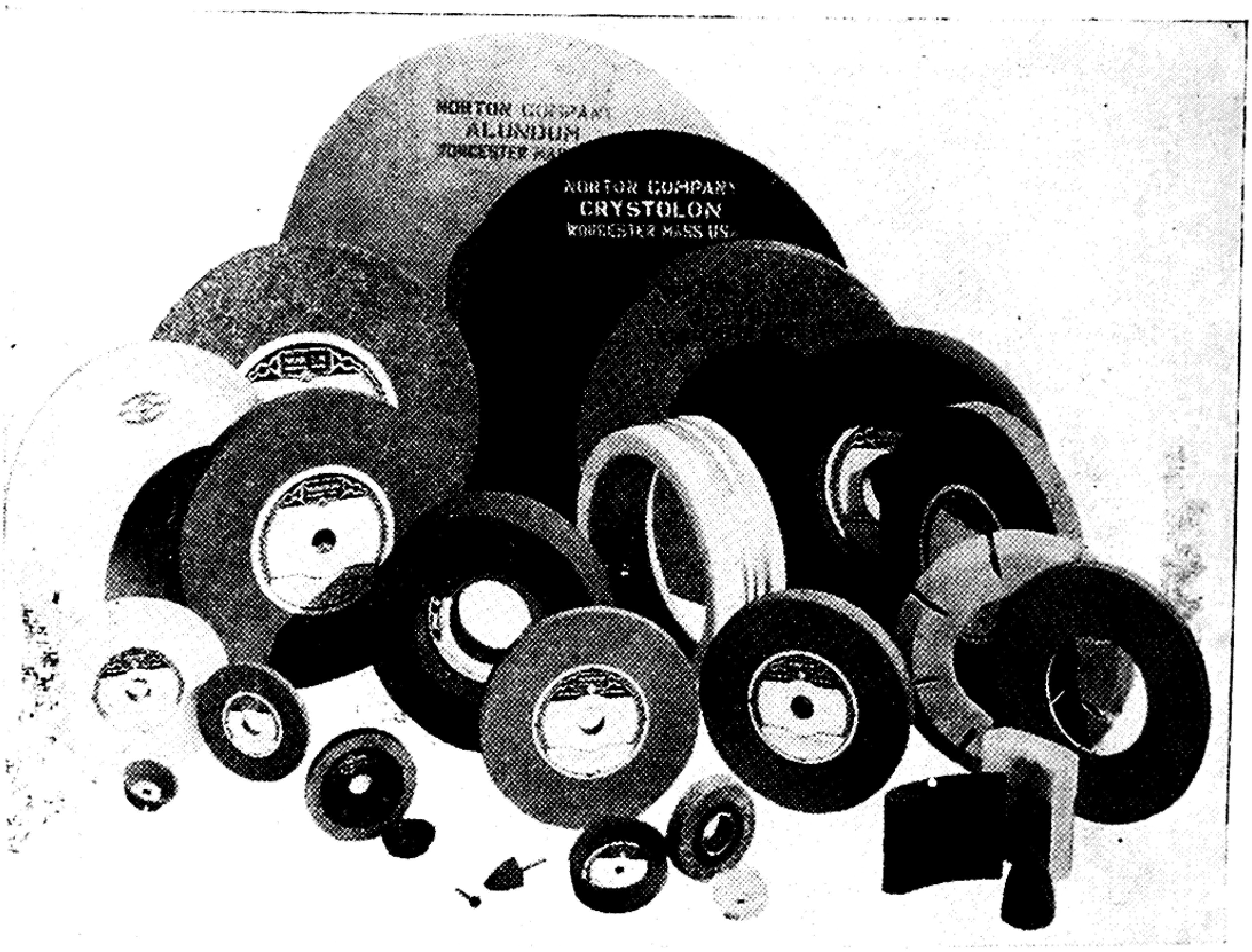

FIG. 2. Grinding wheels are used in a wide variety of shapes and sizes. (*Norton Company.*)

10. Borax (sodium tetraborate), $Na_2B_4O_7 \cdot 10H_2O$, occurs in the Death Valley of California and other desert regions. It is prepared by recrystallization or from related boron compounds. The principal uses of borax are in the manufacture of glass and enamel wares, washing powders, and water softeners. In washing powders, borax produces an alkaline reaction in solution by hydrolysis because tetraboric acid, $H_2B_4O_7$, is a weak acid.

Exercise

6. Write full ionic equations to illustrate the hydrolysis of borax. Give a full explanation of the alkaline reaction.

Borax is also used in *soldering* and *welding*, owing to the fact that it fuses with the oxide impurities on the surface of the metal. Colored glasslike materials are formed by melting borax with various metallic oxides, or salts, as listed in Table III.

TABLE III

Compounds of Metals	*Color of Borax Glass*
Chromium	Green
Cobalt	Blue
Copper	Blue (in oxidizing flame) Red (in reducing flame)
Iron	Brown (in oxidizing flame) Green (in reducing flame)
Manganese	Violet
Nickel	Brown

11. Boric acid (boracic acid), H_3BO_3, is a well-known *antiseptic* commonly used in the treatment of infected eyelids. It is a very weak acid. The common method for preparing boric acid is based upon the reaction of a hot solution of borax with acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 4H_3BO_3\downarrow + 2NaCl$$

When the solution cools, boric acid crystals are formed.

12. Glass. The manufacture of glass dates back to very early times and was, for centuries, regarded as an art. Today, glasses for a wide variety of uses can be made, ranging from camera lenses to the flexible product known as *fiber glass* for window drapes, awnings, etc. Every step in the process of manufacture of glass is under rigid chemical control. The high resistance of modern laboratory glassware to acids and physical shock is well known to laboratory workers. The use of optical glass in spectacle lenses is appreciated by millions of people with defective vision.

13. Ordinary soft glass is made by melting together sodium carbonate, calcium carbonate, and sand. Reactions expressed in simplified form are as follows:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

The finished glass thus contains Na_2SiO_3 and $CaSiO_3$ with additional silica and often smaller amounts of other materials such as Na_2SO_4, B_2O_3, or $Na_2B_4O_7$. *Soft glass* may thus be considered to be composed of the three oxides, SiO_2, Na_2O, and CaO, usually in the proportion, $Na_2O{\cdot}3CaO{\cdot}6SiO_2$. The compositions of special and colored glasses are indicated as in Table IV.

TABLE IV
GLASS COMPOSITION

Name	Composition	Distinctive properties
Window glass, soft glass, plate glass	SiO_2, Na_2O, CaO	Low melting point, cheap
Flint glass, optical glass	SiO_2, K_2O, PbO	Very low melting point, very soft
Hard glass (crown glass)	SiO_2, K_2O, CaO	Hard, brittle, high melting point
Pyrex glass (borosilicate glass)	SiO_2, Na_2O, B_2O_3, CaO	Resistant to etching of alkali solutions. High melting point, hard to break by shock or temperature change
Red glass	SiO_2, Na_2O, CaO, and SeO_2 or Au or Cu_2O	
Blue glass	SiO_2, Na_2O, CaO, and CoO or CuO	
Green glass	SiO_2, Na_2O, CaO, and FeO or Cr_2O_3	
Violet glass	SiO_2, Na_2O, CaO, and MnO	
Brown glass, yellow glass	SiO_2, Na_2O, CaO, and Fe_2O_3	

Any of the above glasses listed in Table IV may contain considerable proportions of other components. *Safety glass* is made by cementing a layer of a transparent plastic material between two layers of ordinary glass. *Optical glass* is usually of special composition and manufacture, depending upon the properties desired. A small amount of chemical apparatus and other equipment is made of fused transparent silica. This is expensive but almost impossible to break by sudden heating or cooling. Enamels and glazes on tile and other ceramic ware are special forms of glass. The etching of glass by hydrofluoric acid should be reviewed (XII. 3).

Exercises

7. Write equations for the reaction of hydrofluoric acid with (*a*) silicon dioxide, (*b*) calcium silicate.

8. (*a*) What is meant by index of refraction? (*b*) What is the relationship between the composition of optical glass and its index of refraction?

9. (*a*) What is meant by coefficient of expansion? (*b*) Would the coefficient of expansion of Pyrex glass be an important factor in the practical use of this glass?

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CHAPTER XXV

LEAD AND SILVER

Laboratory studies in the chemistry of the metals may well include work in the qualitative analysis of the common metallic ions. We shall, therefore, take up the study of the more common metals in approximately the same order in which they are presented in the qualitative analysis. A study of the reactions involved in the analytical work can also be made in the lectures and recitations.

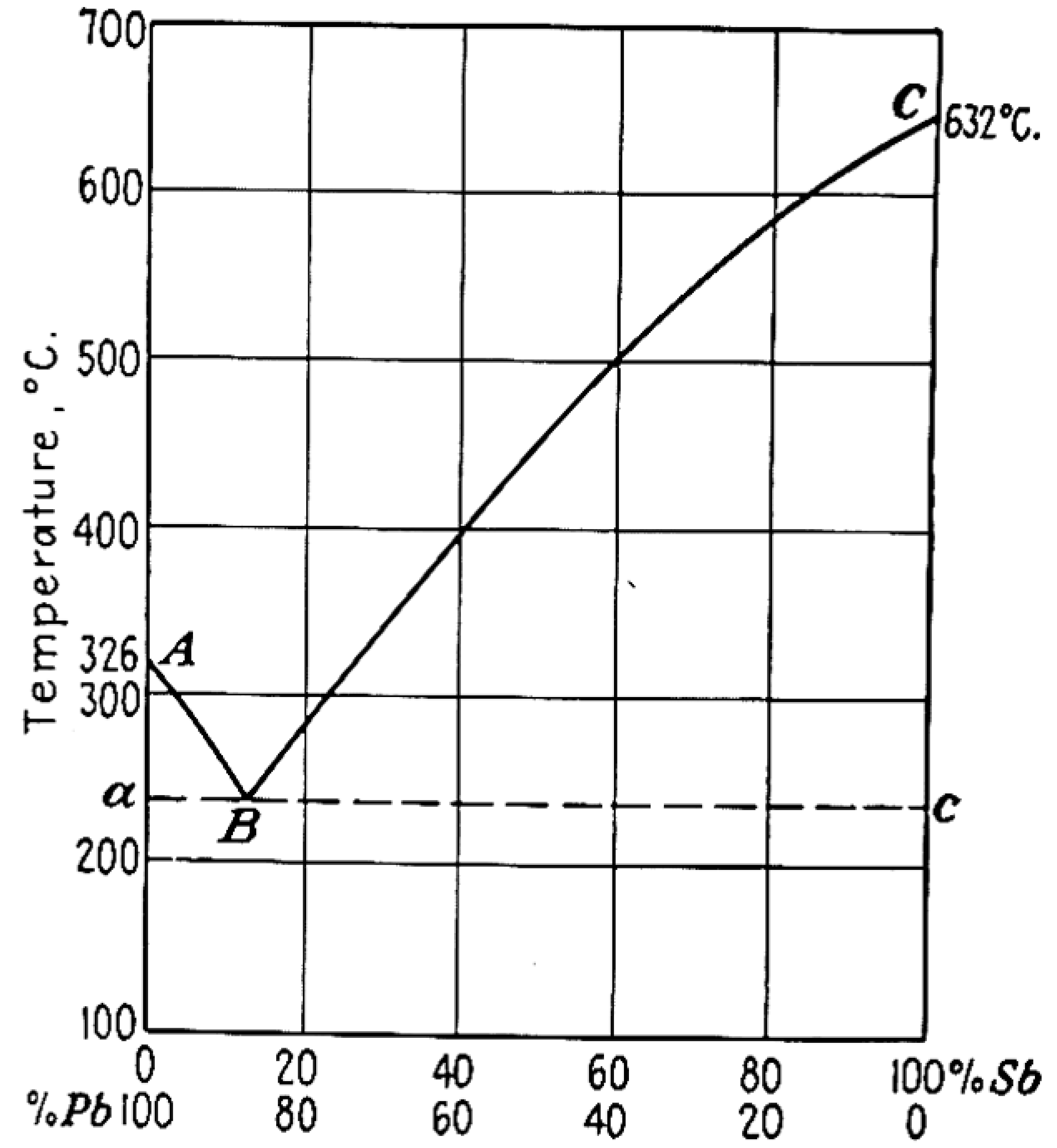


FIG. 1. Melting-point diagram of lead-antimony alloys. (*Kendall, "Smith's College Chemistry," D. Appleton-Century Company, Inc.*, 1935.)

Group I of the qualitative analysis includes the ions of lead, silver, and (mercurous) mercury. In this chapter, we shall consider the metals, lead and silver, and some of their important compounds.

1. Properties and Uses of Lead. Lead is the heaviest, softest, and most flexible of the common metals. It has a relatively low melting point (327°C.) and low chemical reactivity. With certain other metals, lead is used in making alloys of low melting point, *e.g.*, fusible alloys (Wood's metal) for plugs in automatic sprinkler systems, also type metal, solder, and shot. Because of its flexibility and its resistance to corrosion, it is used for making water pipes and telephone cable coverings. Large amounts of lead are used in the manufacture of *white lead* (basic lead carbonate) and the electrodes for storage batteries.

Exercise

1. Alloys of antimony and lead melt at varying temperatures as shown by the melting-point diagram (Fig. 1). From this diagram, state how the melting point varies (increases or decreases) with change in composition (*a*) from 0.0 to 13.0 per cent Sb, (*b*) from 13.0 to 100 per cent Sb; (*c*) how the melting point of the alloy changes by adding lead to antimony. What is the composition (*d*) of the alloy having the minimum melting point? (*e*) of the two possible alloys having a melting point of approximately 300°C.?

2. Occurrence and Metallurgy of Lead. The principal source of lead is galena or lead sulfide, PbS, which occurs naturally in the form of cubic crystals resembling lead in appearance. Galena is found rather abundantly in many parts of the world. To obtain pure lead from this ore, four processes are necessary:

a. Concentration. A treatment commonly used in metallurgy to remove the rock impurities (gangue) from the ore.

b. Roasting. The heating of the ore in air to convert the sulfide ore to lead oxide and sulfur dioxide.

c. Reduction. Heating the lead oxide with carbon, usually coke, forming impure lead and carbon dioxide.

d. Refining by Electrolysis. A process that removes traces of other metals from the impure lead. The Parkes process is also used in refining lead (Sec. 7).

Exercises

2. Write two equations illustrating the roasting and the reduction processes.
3. How many pounds of lead can be obtained from 10 tons of lead sulfide ore containing 90 per cent of rock impurities?

3. Oxides of Lead. Three of these are important (Table I).

TABLE I

Formula	Names	Color	Uses
PbO	Lead monoxide or litharge	Light yellow	Glass manufacture and litharge-glycerin cement
PbO_2	Lead dioxide	Dark red brown	Plates of storage cells
Pb_3O_4	Red lead	Red	Paint pigment, flint glass

4. Other Lead Compounds. Various other compounds of lead are listed in Table II.

TABLE II

Name	Formula	Use
White lead	$Pb(OH)_2 \cdot 2PbCO_3$	Base or body for paints
Chrome yellow or lead chromate	$PbCrO_4$	Paint pigment
Lead tetraethyl	$Pb(C_2H_5)_4$	Antiknock agent in motor fuel
Galena	PbS	Lead ore, rectifier
Lead arsenate	$Pb_3(AsO_4)_2$	Insecticide

5. Paints. Large amounts of lead compounds are used in paint manufacture. Paints generally contain four components: (1) the oil, (2) the base or body, (3) pigment, (4) a drier. The oil is usually linseed oil, but other oils are coming into use. The most common base is white lead although lithopone, $BaSO_4 + ZnS$, is also used. Driers are usually complicated organic compounds of cobalt or manganese. There is little or no evaporation during the drying of a paint. The principal change is the oxidation of the oil to a hard resinous film. The drier acts as a catalyst and hastens the oxidation and formation of the film. The body or base gives covering power and the pigment gives color to the paint.

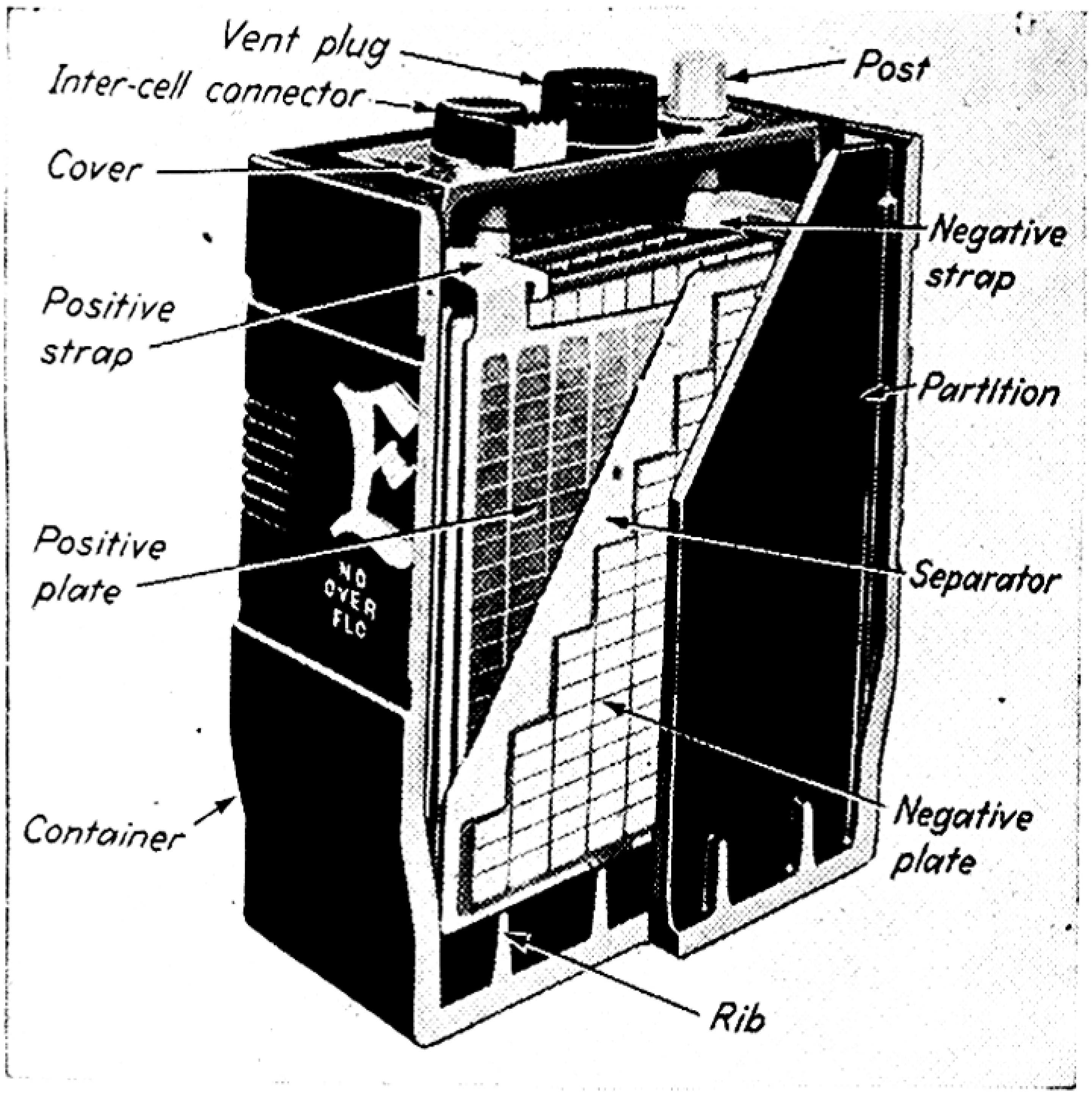
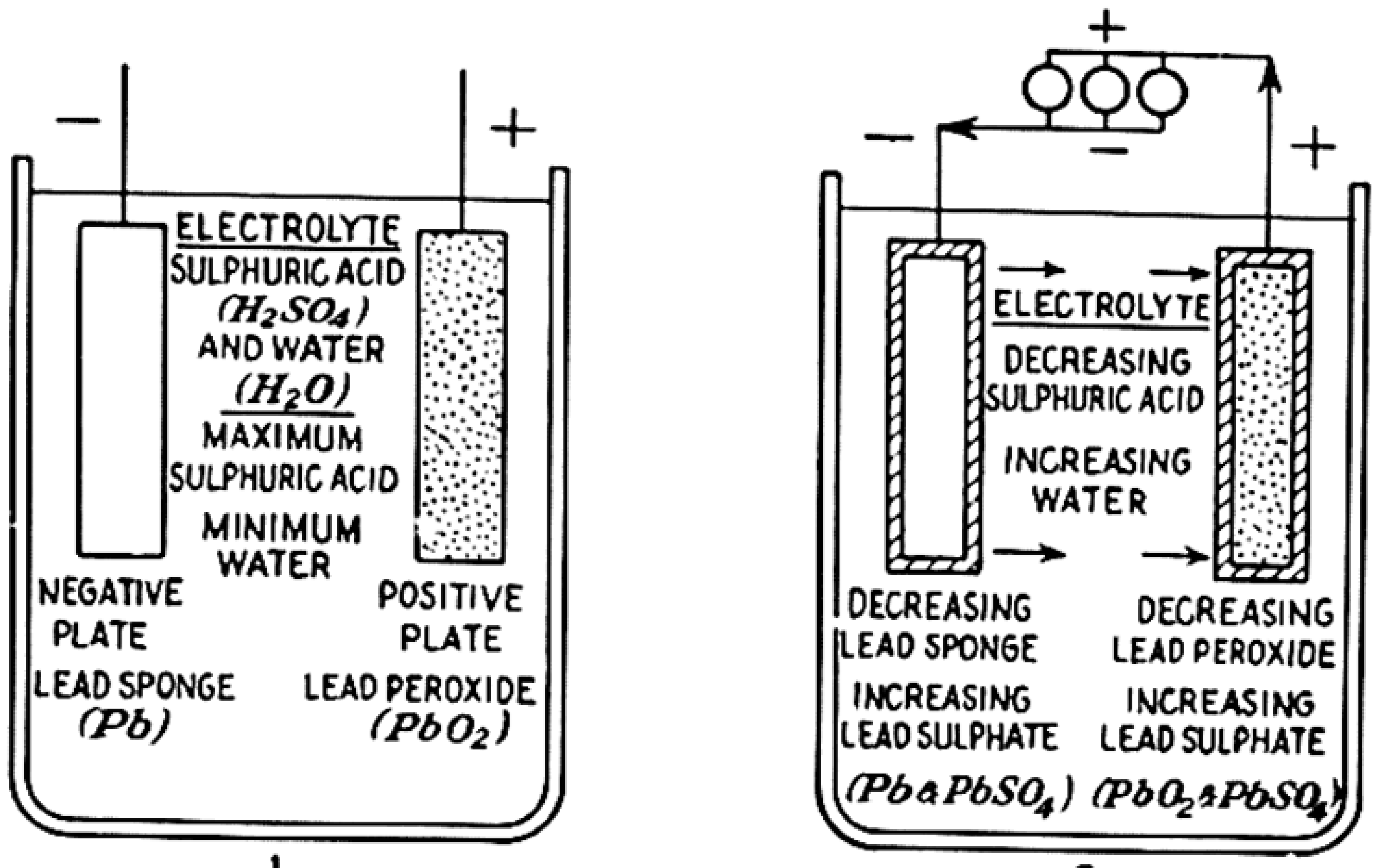


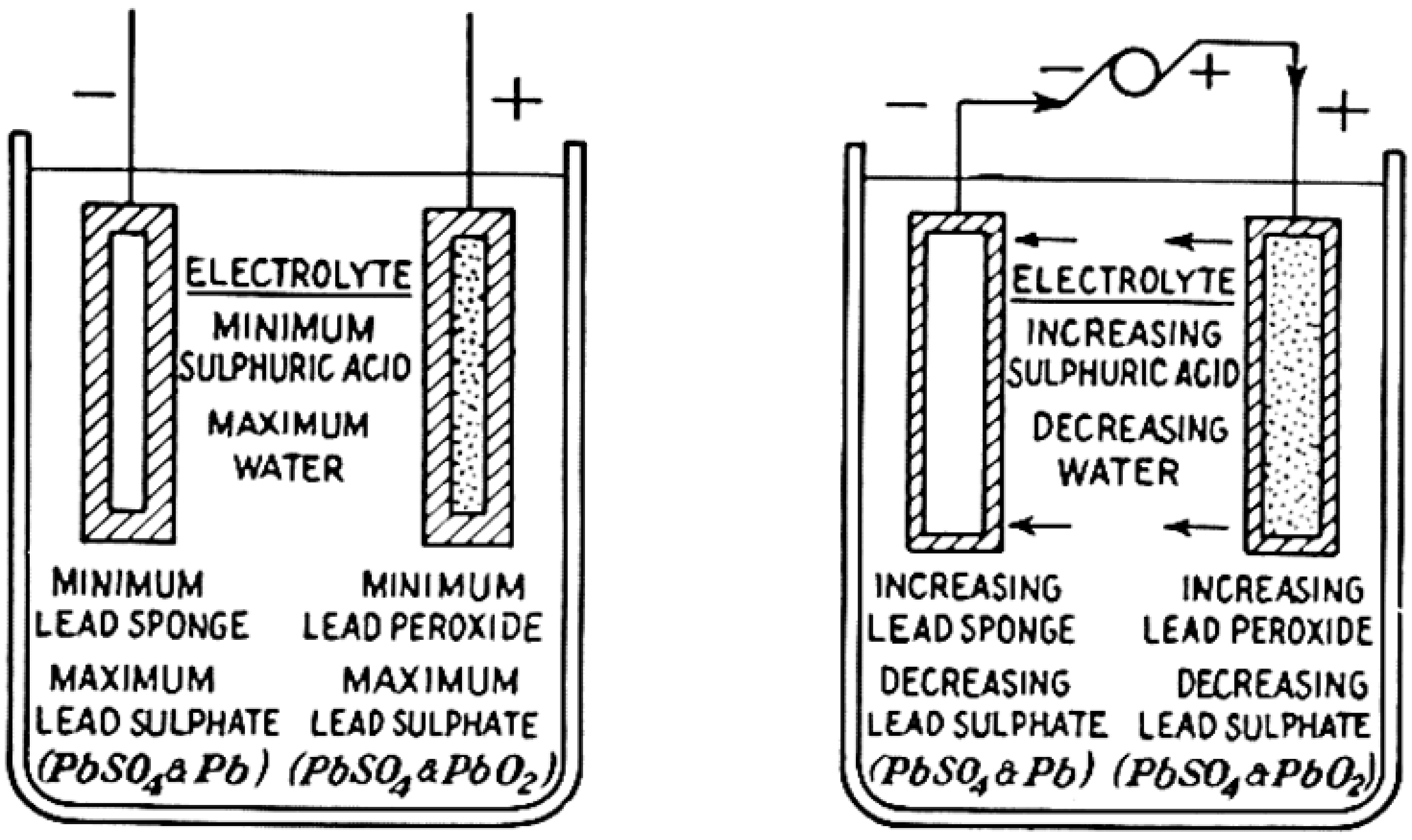
FIG. 2. A lead-plate storage cell. (*The Electric Storage Battery Company.*)

6. Lead-plate Storage Cell. Any battery of this type in actual use has Pb and $PbSO_4$ on one set of plates, while PbO_2 and $PbSO_4$ are present on the other plates. The liquid or electrolyte is water and sulfuric acid. The specific gravity of the electrolyte of a charged cell is about 1.3. As the cell becomes discharged, the specific gravity decreases to a lower value. The general construction of a lead-plate storage cell is illustrated in Fig. 2. The materials on the electrodes,



1
CHARGED

2
DISCHARGING



3
DISCHARGED

4
CHARGING

Fig. 3. Charged and discharged lead-plate storage cell. (*The Electric Storage Battery Company.*)

with connections to a motor and a generator, are indicated in Fig. 3.

A fully charged cell has little if any $PbSO_4$ on either plate, this being formed simultaneously on both plates by the following mechanism:

When current is drawn from the cell by closing a switch, the battery is discharged. During this process SO_4^{--} ions go to the Pb plate.

$$Pb^\circ + SO_4^{--} - 2e^- \rightarrow PbSO_4 \qquad (1)$$

The electrons pass away through the wire, through the lamps, and back to the PbO_2 plate. At this plate the electrons are used in the following reaction:

$$PbO_2 + 4H^+ + SO_4^{--} + 2e^- \rightarrow PbSO_4 + 2H_2O \qquad (2)$$

It is to be emphasized that reactions (1) and (2) occur simultaneously. Thus, the total reaction is

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2PbSO_4 + 2H_2O \qquad (3)$$

and of course, also, the flow of electrons (electric current) causes the lamps to glow. Thus, the chemical energy of the PbO_2, Pb, and H_2SO_4 is converted into heat and light energy in the lamps. Any other electrical device can be substituted for the lamps.

Eventually the battery must be recharged. This is done by closing a switch so that the generator can drive electrons from the PbO_2 plate to the Pb plate. It is to be noted that this electron stream is in the direction opposite to that during the discharge. As a result, both of the above reactions are reversed and the $PbSO_4$ is converted back to Pb on one plate, to PbO_2 on the other, and SO_4^{--} ions are returned to the solution.

Exercise

4. Give two reasons why the specific gravity of the electrolyte of the lead-plate storage cell decreases as the cell is being discharged. Write ion-electron equations for the reactions in this cell.

SILVER

7. Occurrence and Metallurgy. Nuggets and veins of metallic silver are found in certain rock formations. It is usually mixed with copper and gold. Silver sulfide, Ag_2S, known as *argentite*, an important natural ore of silver, is usually found mixed with sulfides of lead, copper, nickel, and other metals.

Most of the silver produced is obtained as a by-product in the smelting of lead, copper, and nickel ores. Silver is separated from impure lead by means of the *Parkes process* in which zinc is melted with the lead. The silver is more soluble in the zinc, which floats and can be skimmed off the top. By heating the zinc-silver mixture in a retort, the zinc is removed by distillation and can be used over again.

8. Properties and Uses. Silver possesses a high reflecting property toward light and, as a conductor of heat, it ranks first among the metals. It is quite malleable and soft and consequently does not wear well. The principal use as a metal is in making coins, jewelry, and tableware. Silver coins of the United States contain 10 per cent copper and 90 per cent silver. Dental alloys and mirrors also require large amounts of silver.

As every housewife knows, silverware in contact with foods containing sulfur becomes tarnished, or coated with a dark stain of silver sulfide. A common method of removing this stain is to place the silverware in an aluminum dish containing about a teaspoonful of salt and the same amount of baking soda, per quart of water. The silver sulfide dissolves forming silver ion, Ag^+, which is discharged by the aluminum metal, and a fresh film of silver is deposited upon the surface of the ware. The equation for the reaction is

$$Al + 3Ag^+ \rightarrow Al^{+++} + 3Ag$$

The sulfide ions are of course discarded in the rinsing water.

Exercise

5. What are the relative positions of the aluminum and silver in the activity series? Indicate the gain and loss of electrons in the above equation.

9. Important Compounds of Silver. Silver nitrate, $AgNO_3$, is made in large quantities by dissolving silver in nitric acid and evaporating the water until the solid salt is crystallized out of the solution.

Exercises

6. Write the equation for the reaction of silver with dilute nitric acid, assuming that nitric oxide, NO, is formed.
7. Calculate the weight of silver nitrate that is formed from 10 lb. silver, by the above reaction.

Silver halides, AgCl (white), AgBr (pale yellow), AgI (yellow), are prepared in large quantities from silver nitrate by the photographic industry. These compounds are used in making photographic plates and films because of their high sensitivity to light.

10. Photography. The chemical principles of photography, briefly stated, are the following: The plate or film containing the silver halide when exposed to light is affected by the light so that the silver ion can be reduced by the developer (hydroquinone, etc.). Silver, in finely divided form, is deposited upon the plate or film, the quantity depending upon the intensity of the light. Thus, light objects appear darkest on the negative.

Unaffected areas of silver halide, AgBr, are then dissolved by "fixing" with *hypo* or sodium thiosulfate while the film is kept in the dark room. Printing is accomplished by exposing another film to this negative, thus reversing the dark and light areas. When this film is developed, it bears a true image of the original object. Larger textbooks or a special treatise should be consulted for details of the process.

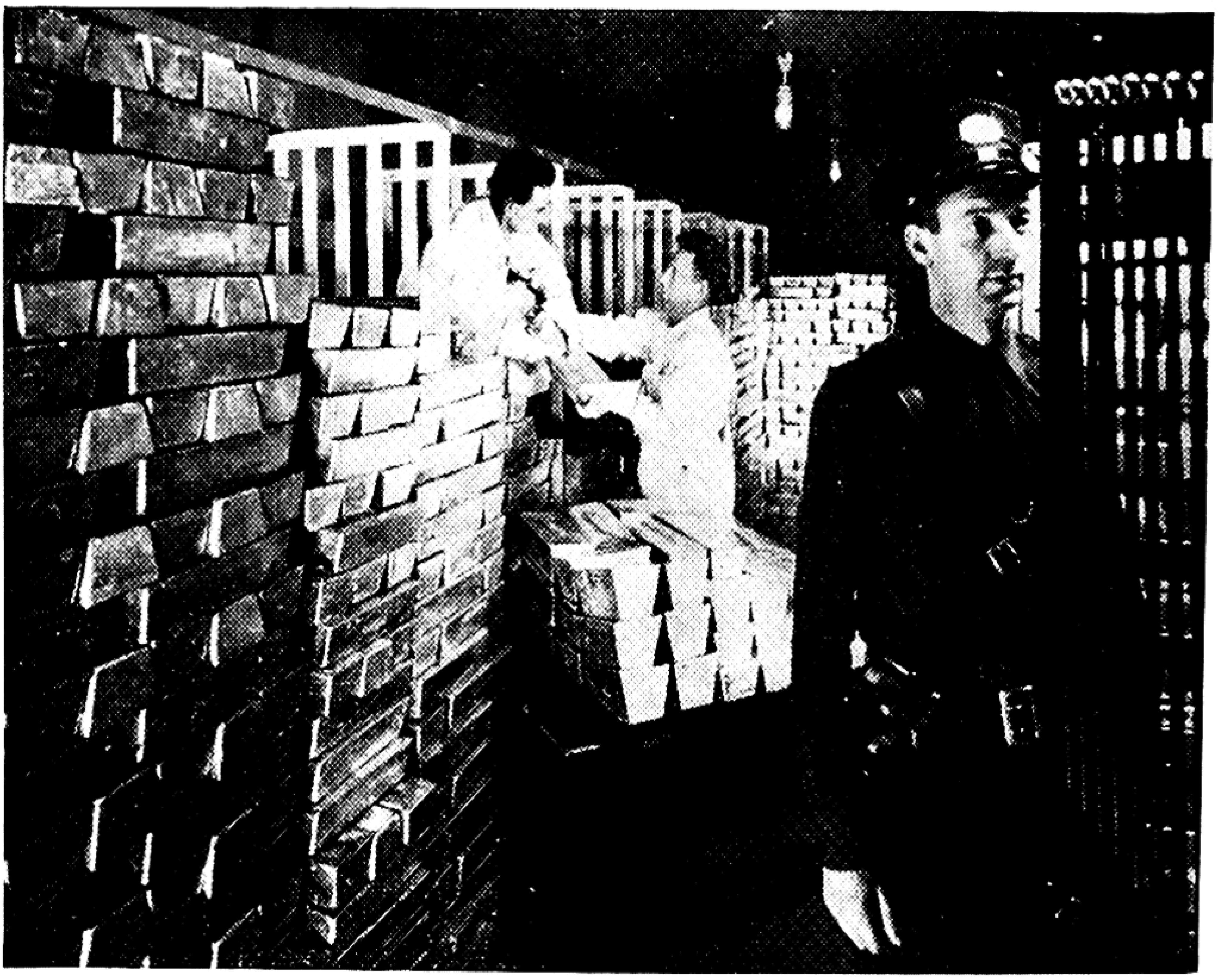


FIG. 4. Silver for the photographic industry. There is a ton of silver on the truck.

Exercises

8. Outline the main steps involved in the photographic process.

9. Write three ionic equations for the reactions involved in the separation and identification of silver ion in Group I of qualitative analysis.

10. Write two ionic equations for the reactions involved in the separation and identification of lead ion in Group I of qualitative analysis.

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CHAPTER XXVI

MERCURY AND COPPER

The metals, mercury and copper, resemble each other in several respects. Both occur naturally as sulfides as well as in the free state, and both form two series of compounds in which the valence numbers are 1 and 2. In the activity series, both metals are below hydrogen.

1. Occurrence and Metallurgy of Mercury. The principal ore is *cinnebar* or mercuric sulfide, HgS. This ore occurs in the form of red deposits on rock which is crushed and heated in a furnace. When the concentrated ore is heated in excess of air (roasting), the sulfur is converted to sulfur dioxide and the mercury vapor is condensed to the liquid metal which is collected in iron flasks.

Before the Second World War, Italy and Spain produced most of the world's supply of mercury. When these sources were no longer accessible, the United States and Mexico began to supply the market.

2. Properties. Mercury is the only metal in the liquid state at ordinary temperature. Because of its low freezing point (−39°C), high specific gravity (13.6), and low vapor pressure, it is the principal material used for filling thermometers and barometers. Mercury is dissolved by nitric acid but not by hydrochloric or sulfuric acids.

Exercise

1. Write an equation for the reaction of mercury (*a*) with dilute nitric acid, (*b*) with concentrated nitric acid.

3. Amalgams are alloys (solutions, compounds, or mixtures) of mercury and one or more other metals. They may be solid or liquid.

Sodium amalgam is formed in the process for the manufacture of metallic sodium, while gold amalgam is formed in the recovery of gold from certain ores. Amalgams of tin, silver, gold, etc., are used by dentists for filling teeth.

4. Mercury Compounds. Various compounds of mercury are listed in Table I.

Table I

Names	Formulas	Uses
Calomel, or mercurous chloride	Hg_2Cl_2	Liver stimulant
Corrosive sublimate, or bichloride of mercury	$HgCl_2$	Poison, germicide, fungicide
Fulminate of mercury	$Hg(CNO)_2$	Detonator, percussion caps
Nessler's reagent, or potassium mercuric iodide	K_2HgI_4	Used in testing for traces of ammonia
Vermillion or mercuric sulfide	HgS	Red pigment
Mercury amido chloride	$HgNH_2Cl$	Ointments

5. Some Reactions of Mercury Ions, Hg^+ and Hg^{++}.

$$Hg^+ + Cl^- \rightarrow HgCl,\ Hg_2Cl_2 \qquad \text{(mercurous chloride is insoluble in water)} \tag{1}$$

or

$$Hg^{++} + S^{--} \rightarrow HgS \tag{2}$$

$$HgS + \underset{\text{aqua regia}}{HNO_3 + HCl} \rightarrow HgCl_2 + S + NO + H_2O \tag{3}$$

Exercises

2. Balance Eq. (3) by gain and loss of electrons. What kind of reaction is it?

$$HgCl_2 + \underset{\text{stannous chloride}}{SnCl_2} \rightarrow \underset{\text{white}}{HgCl\downarrow} + SnCl_4 \tag{4}$$

$$HgCl + SnCl_2 \rightarrow \underset{\text{black}}{Hg\downarrow} + SnCl_4 \tag{5}$$

3. Balance Eqs. (4) and (5) by gain and loss of electrons. What type of reactions are these? (These are the reactions used in qualitative analysis for the identification of mercuric ions.)

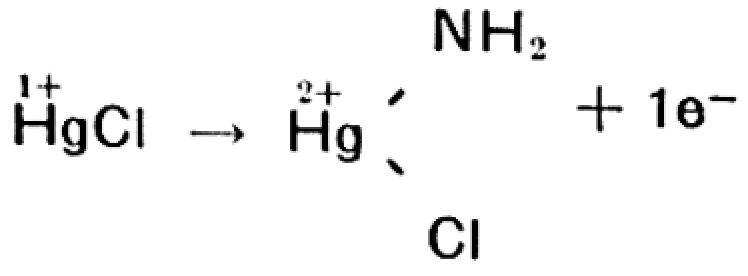
An interesting and rather complicated reaction is that of mercurous chloride with ammonium hydroxide, which is used to identify mercurous chloride in Group I.

$$\underset{(Hg_2Cl_2)}{2HgCl} + 2NH_4OH \rightarrow \underset{\text{white}}{HgNH_2Cl} + \underset{\text{black}}{Hg} + NH_4Cl + 2H_2O \tag{6}$$

or

$$2HgCl + 2NH_3 \rightarrow \underset{\text{mercuric amido chloride}}{HgNH_2Cl} + Hg + NH_4Cl \tag{7}$$

The two mercurous ions undergo mutual oxidation and reduction as indicated by the following equations:



$$\overset{1+}{HgCl} \rightarrow \overset{2+}{Hg}\left\langle\begin{matrix}NH_2\\ Cl\end{matrix}\right. + 1e^-$$

$$\overset{1+}{HgCl} + 1e^- \rightarrow Hg^\circ + Cl^-$$

COPPER

6. Occurrence and Metallurgy of Copper. In the Lake Superior region, copper is found abundantly in the native or uncombined state. In the Rocky Mountain deposits (Montana, Utah, and Arizona) the principal ores are the sulfides, *chalcopyrite*, $Cu_2S{\cdot}Fe_2S_3$ or $CuFeS_2$, and *chalcocite*, Cu_2S. The removal of copper from these ores is a complex process. The details of the process, depending upon the type of ore, involve several operations which in principle may be described as follows:

a. Concentration. Low-grade ores are finely crushed and treated with an oil and water. The copper ore is preferentially wetted by the oil and floats on the surface (oil flotation) while the gangue or siliceous material is wetted by the water and collects in the water layer. The ore concentrate is then skimmed off and, from this material, pure copper is obtained by the following processes:

b. Roasting or Heating in a Furnace with an Excess of Air. Some of the sulfur is removed by oxidation, which converts a part of the iron in $CuFeS_2$ to FeO. The reaction may be indicated as follows:

$$2CuFeS_2 + 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2$$

The residue or "calcine" from the roasting furnace is essentially a mixture of Cu_2S, FeS, FeO, and SiO_2 (impurity).

c. Slagging (Smelting). The calcine from the roasting furnace is heated with limestone which acts as a *flux*. The calcium oxide from the limestone and the ferrous oxide react with the silica forming *slag* which is drawn off in the molten state and discarded. The equations are as follows:

$$\underset{\text{limestone}}{CaCO_3} \rightarrow CaO + CO_2$$

$$\left.\begin{matrix}CaO + SiO_2 \rightarrow CaSiO_3\\ FeO + SiO_2 \rightarrow FeSiO_3\end{matrix}\right\}\text{slag}$$

d. Reduction. The remaining mixture of Cu_2S and FeS, called *matte*, is then heated in a reduction furnace or converter (1) to remove the residue of iron sulfide (by oxidation and slagging) and (2) to reduce the cuprous sulfide. The reactions are as follows:

$$\begin{aligned} 2Cu_2S + 3O_2 &\rightarrow 2Cu_2O + 2SO_2 \\ Cu_2S + 2Cu_2O &\rightarrow 6Cu + SO_2 \end{aligned}$$

(Note that the oxide and the sulfide of copper are both reduced.) Final reduction of Cu_2O is done by placing poles of wood in the molten metal. The carbon and carbon monoxide from the wood react with the Cu_2O as follows:

$$\begin{aligned} Cu_2O + C &\rightarrow 2Cu + CO \\ Cu_2O + CO &\rightarrow 2Cu + CO_2 \end{aligned}$$

The impure copper known as *blister copper* contains other metal impurities and must be refined by electrolysis.

7. Electrolytic Refining of Copper. Even very small percentages of impurities make copper unsuitable as an electrical conductor because of increased electrical resistance. The impurities usually present are silver, gold, iron, and nickel. These are removed by electrolytic refining. In this process, bars of impure copper (anodes) and thin sheets of pure copper (cathodes) are placed in a bath of copper sulfate solution. When a direct current is passed through this arrangement, copper and more active metals dissolve from the impure bar, while only pure copper plates-out on the thin sheets. The metals less active than copper, platinum, silver, and gold, do not dissolve but finally fall to the bottom of the bath as *anode mud.* For the process to be satisfactory, the voltage must be properly controlled (0.4 volt). Too high voltage will cause all the metals to dissolve and plate-out together. With too low voltage, no plating will occur. The reactions are as follows:

At the anode of impure copper:	At the cathode of pure copper:
$Cu^\circ \rightarrow Cu^{++} + 2e^-$	$Cu^{++} + 2e^- \rightarrow Cu^\circ$
$Fe^\circ \rightarrow Fe^{++} + 2e^-$	
$Zn^\circ \rightarrow Zn^{++} + 2e^-$	
$Ni^\circ \rightarrow Ni^{++} + 2e^-$	
Pt → no action	
Ag → no action	
Au → no action	

The electrons produced at the anode are forced through the external electrical circuit by the generator and, in turn, these electrons are used at the cathode. The positive copper ions migrate away from the anode (+) toward the cathode (−). The sulfate ions remain in the solution.

The anode mud is removed and treated to recover the noble metals that it contains. The copper sulfate solution must be removed from time to time so that it can be purified of iron, zinc, nickel, and similar metals.

Exercise

4. Construct a labeled diagram for the electrolytic copper refining process so as to represent all the essential materials and changes.

8. Properties and Uses of Metallic Copper. Copper has a high electrical conductivity, a high heat conductivity, and a considerable resistance to corrosion, as well as relatively high tensile strength. Its electrical uses are well known. Pure copper is also often used for kettles and other containers used for heating and boiling liquids. This use depends upon its high heat conductivity and resistance to corrosion. Copper is present in common alloys such as brass, bronze, and monel metal, which has an unusually high resistance to corrosion and a low heat conductivity. A small percentage of copper in steel increases its resistance to corrosion.

9. Bordeaux Mixture. This widely used spray material is prepared by mixing a solution of copper sulfate with lime in the proper proportions. In the reaction, a bluish-white insoluble suspension is formed according to the equation

$$CuSO_4 + Ca(OH)_2 \rightarrow \underset{\text{blue}}{Cu(OH)_2} + \underset{\text{white}}{CaSO_4}$$

This mixture is generally prepared just before using and is sprayed upon potatoes and other crops to kill blight and certain insects. (Details may be obtained from agricultural experiment station bulletins.)

10. Fehling's Solution and Benedict's Solution. These solutions are essentially alkaline solutions of copper ion, Cu^{++}, and are used by clinical laboratories in testing for reducing sugars, *e.g.*, glucose, in urine. Such tests are necessary in the diagnosis of diabetes, a disease of the kidneys. A positive test for the presence of the reducing sugar is the precipitation of bright red (or yellow) cuprous oxide, Cu_2O. Note that the cupric ion is reduced, $Cu^{++} \rightarrow Cu^{+}$ (in Cu_2O). *Fehling's solution* is made up in two separate containers: (1) solution of copper sulfate and (2) solution of sodium potassium tartrate and sodium hydroxide. The two solutions are mixed at the time when the test is made. *Benedict's solution* is a single solution of copper sulfate, sodium citrate, and sodium carbonate. Because it is stable and more convenient to use, Benedict's solution has replaced Fehling's solution in many laboratories.

11. Some Reactions of Copper and Copper Ion. The metal, copper, will not displace hydrogen from hydrochloric acid, since it is below hydrogen in the activity series. With hot concentrated sulfuric acid, copper forms copper sulfate, sulfur dioxide, and water. The sulfuric acid when hot and concentrated is an oxidizing agent. Nitric acid, both dilute and concentrated, also reacts with copper.

When a solution of copper sulfate is evaporated, the hydrate, $CuSO_4{\cdot}5H_2O$, called *blue vitriol*, is crystallized out. This hydrate, when heated, loses the combined water, forming white anhydrous copper sulfate (dehydration). If anhydrous copper sulfate is placed in alcohol containing only a small percentage of water, a blue color will be observed which constitutes a test for traces of water in a sample of alcohol or other liquid.

Copper ion is readily precipitated by hydrogen sulfide, forming black copper sulfide which is soluble in dilute nitric acid. The equations for these reactions are as follows:

$$Cu^{++} + S^{--} \rightarrow CuS$$

skeleton form

$$CuS + \underset{\text{dilute}}{HNO_3} \rightarrow Cu(NO_3)_2 + S + NO + H_2O$$

Exercises

5. Write equations for the reaction of copper (*a*) with hot concentrated sulfuric acid, (*b*) with concentrated nitric acid. Indicate what substances are oxidized and reduced in each case.

6. Calculate the weight of water lost in the dehydration of 100 lb. $CuSO_4{\cdot}5H_2O$.

7. Balance the equation for the reaction of copper sulfide with nitric acid. What substance is oxidized and what substance is reduced?

When ammonium hydroxide is added in excess to a solution containing cupric ions, a beautiful deep blue color is produced, owing to the formation of the *complex copper ammonia ion*, $Cu(NH_3)_4^{++}$, also known as the *tetrammino copper ion*. This is a very characteristic test for the presence of cupric ions in a solution. When the ammoniacal solution is acidified, the complex ion is decomposed. The equations are as follows:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$
$$Cu^{++} + 4NH_3 \rightarrow Cu(NH_3)_4^{++}$$
$$Cu(NH_3)_4^{++} + 4H^+ \rightarrow Cu^{++} + 4NH_4^+$$

The cupric ion also reacts with the ferrocyanide ion from potassium ferrocyanide, $K_4Fe(CN)_6$, forming insoluble reddish-brown cupric ferrocyanide, as follows:

$$2Cu^{++} + Fe(CN)_6^{----} \rightarrow Cu_2Fe(CN)_6$$

With sodium hydroxide, cupric ion forms cupric hydroxide, a light blue gelatinous substance, which is readily converted by heating to black cupric oxide, as illustrated by the following equations:

$$Cu^{++} + 2OH^- \longrightarrow Cu(OH)_2$$
$$Cu(OH)_2 \underset{\text{heat}}{\longrightarrow} CuO + H_2O$$

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CHAPTER XXVII

IRON AND STEEL

Among the common metals, iron ranks first in industrial importance. Steel, which is impure iron containing small amounts of carbon and other elements, is a most essential industrial material.

1. Occurrence of Iron. Although iron ranks as the fourth metal in abundance in the earth's crust, it is believed that the core of the earth is composed largely of iron. There are three important ores of iron: hematite, Fe_2O_3; magnetite, Fe_3O_4; and limonite, $2Fe_2O_3 \cdot 3H_2O$.

Exercise

1. Calculate the percentage of iron in each of these oxides.

Hematite is a red oxide which is found abundantly in the Lake Superior region (Michigan and Minnesota). The red color of certain soils and rocks is due to the presence of hematite. Magnetite is a black oxide and, as the name implies, it has magnetic properties. Large deposits of magnetite and hematite are found in the Appalachian range from New York State to Alabama. In the early years of the iron industry, Pennsylvania deposits were worked extensively. The richer deposits of the Lake Superior region have been more profitable as a source of iron and so, in recent years, the industry has shifted westward. Some of the iron furnaces erected in central Pennsylvania during the Revolutionary War period are still in existence.

2. Reduction of Iron Ore. Blast Furnace. Iron ore mixed with coke and limestone, in calculated amounts, is placed in a tall cylindrical furnace with sloping walls, known as a *blast furnace*, so named because hot air is blown into the furnace to convert the coke to oxides of carbon and to produce the heat required for some of the reactions. The structure of a modern blast furnace is shown in Figs. 1 and 2. The height of the blast furnace varies from 75 to 100 ft., and the maximum diameter is about 25 ft. Air is preheated in tall cylindrical chambers called *stoves* containing firebrick which are heated by burning gas from the blast furnace. The hot air, under pressure, is blown into the lower part of the furnace through tubes called *tuyeres*.

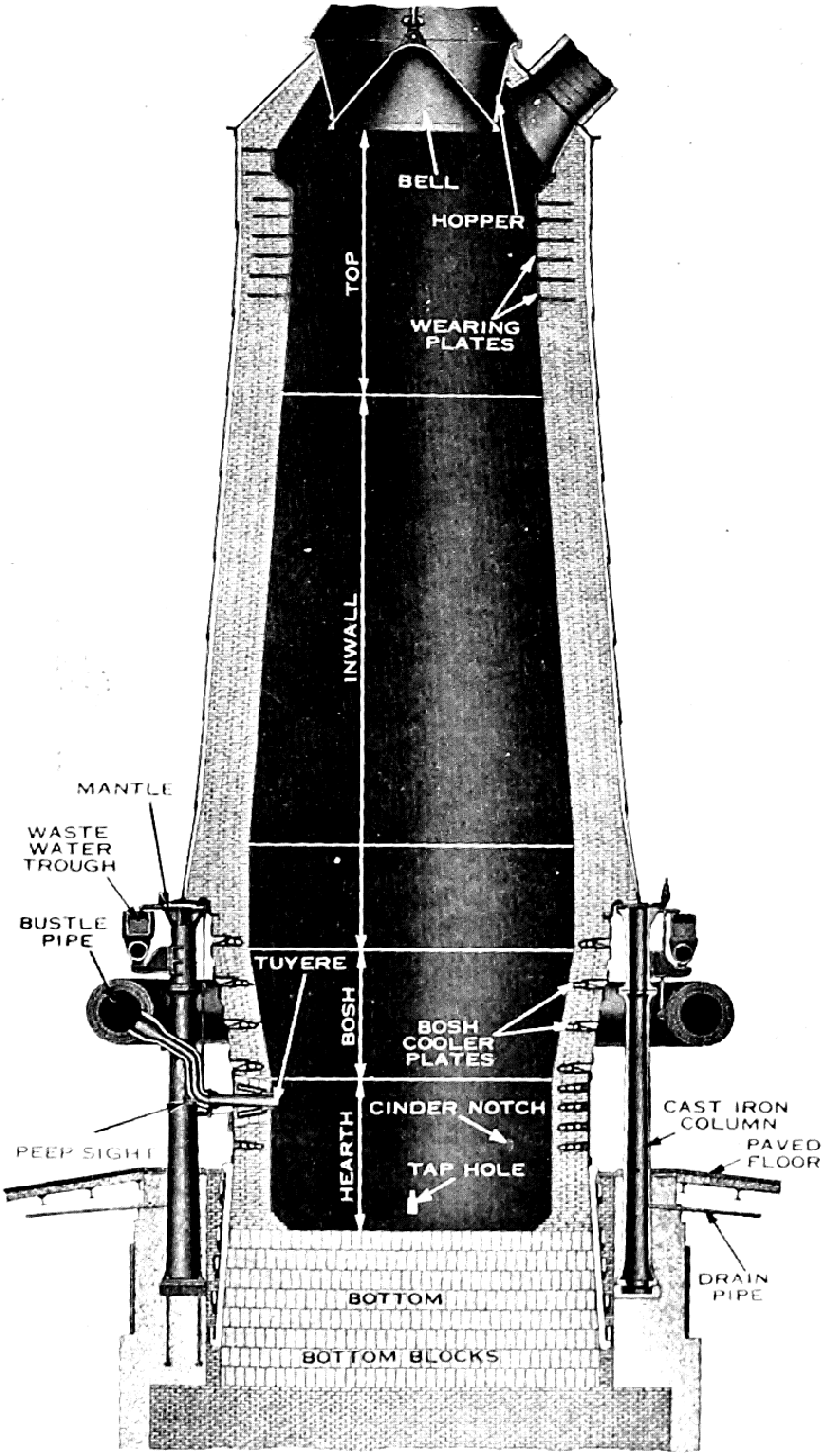

Fig. 1. Cross section of a modern blast furnace. (*Harbison-Walker Refractories Company.*)

The principal chemical reactions that occur in the blast furnace are as follows:

The hot blast of air entering the base of the furnace causes the coke to burn to carbon dioxide and raises the temperature to about 2000°C.

$$C + O_2 \rightarrow CO_2$$

The carbon dioxide in passing upward through the hot coke is reduced to carbon monoxide.

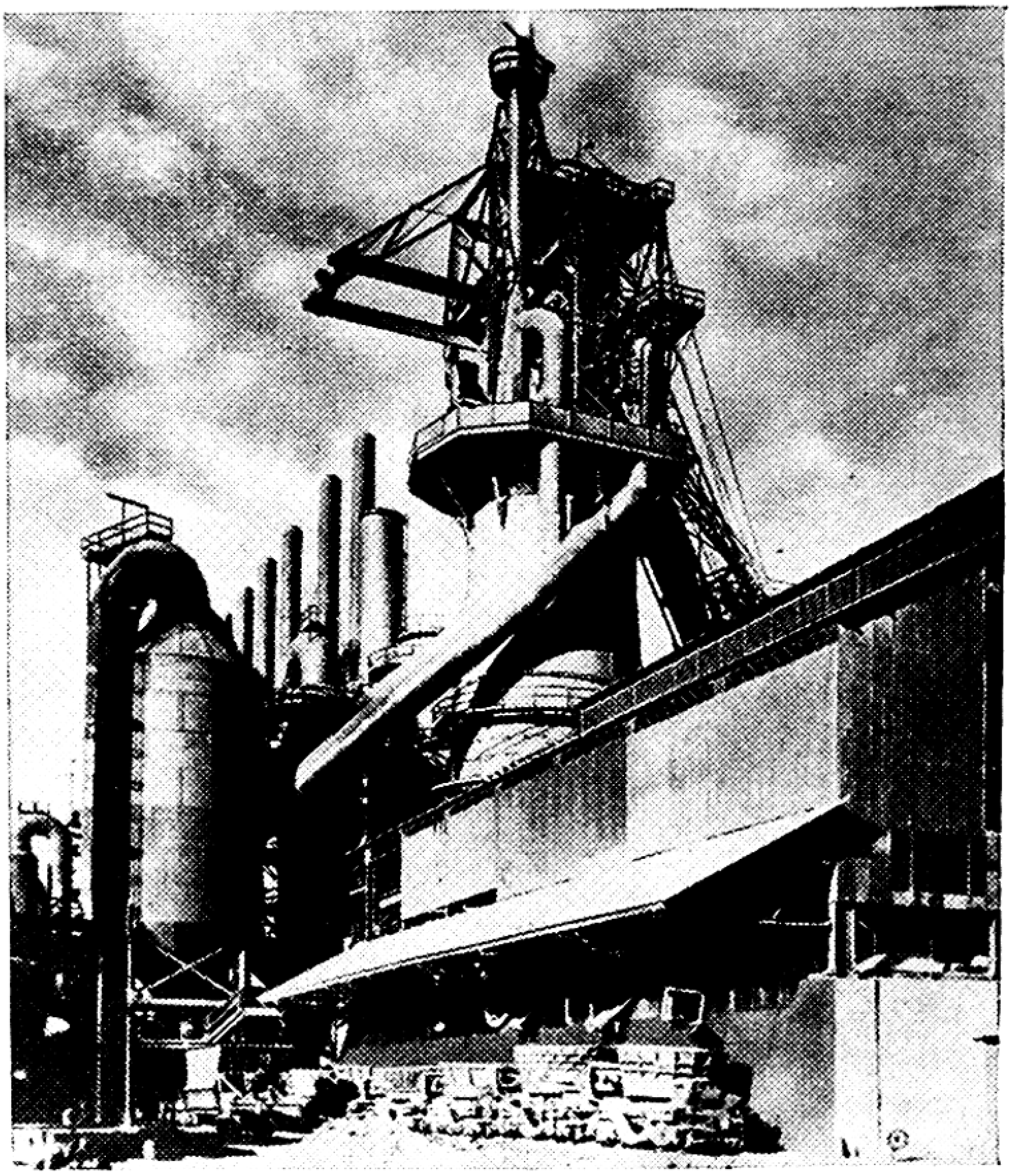

FIG. 2. External view of a modern blast furnace. (*Republic Steel Corporation.*)

$$CO_2 + C \rightleftarrows 2CO$$

The ore is reduced by the carbon monoxide to iron in a series of reactions in the upper part of the furnace.

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$$
$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2$$

The limestone (*flux*), decomposed by heat near the center of the furnace, supplies calcium oxide which combines with the sand or silicate rock in the ore and forms *slag*.

$$CaCO_3 \rightleftarrows CaO + CO_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

All iron ores are admixed with more or less rock. This rock may be essentially calcium or magnesium carbonate, or it may contain considerable sand or silicate rock. The flux used in a blast furnace aids in the separation of the rocklike materials from the iron. This may be accomplished because at high temperatures any basic oxide (metallic oxide) will unite with any acidic oxide (nonmetallic oxide) to form an easily fusible slag that will float upon, but not mix with, the molten iron at the base of a blast furnace. The flux must be properly chosen in order that slag formation will occur.

The molten iron is drawn off at the bottom of the furnace, and the molten slag is drawn off at a slightly higher level. Slag may be rejected or it may be used in road construction or in the manufacture of portland cement.

The gases that are drawn off at the top of the furnace are CO, CO_2, and N_2 from the air blast. The mixture, known as *blast-furnace gas*, is used for preheating the air, as previously described, and for power.

The raw materials and products of the blast-furnace process may now be summarized.

Raw Materials		*Products*
Iron ore, Fe_2O_3	Charge	Cast iron, Fe + C, etc.
Coke, C		Slag, $CaSiO_3$
Limestone, $CaCO_3$		Gas, CO, CO_2, N_2
Air, O_2, N_2		

Exercises

2. Which of the blast-furnace reactions are indicated as reversible? What factors control the reversibility?

3. An ore contains much admixed limestone. What should be used as flux in this case? Write equations for the reactions that occur.

4. Why is the heating value of blast-furnace gas lower than that of water gas?

5. (*a*) Construct a neat diagram showing the shape and materials of construction of a blast furnace.

(*b*) Indicate the four raw materials and their points of entry into the furnace.

(*c*) Indicate the three products, their composition, and points of removal.

6. Write equations showing the formation of each of the substances formed in a blast furnace.

3. Cast Iron. The iron produced in the blast furnace contains from 2 to 4.5 per cent carbon and varying amounts of silicon, manganese, phosphorus, and sulfur. Because of these impurities, cast iron is quite brittle and of low tensile strength. These properties limit the use of cast iron to the construction of articles that are not likely to sustain mechanical stress or shock, *e.g.*, machine bases, radiators, stoves, and window weights. The molten iron upon removal from the blast furnace may be cast into bars known as *pig iron* or transferred while hot to an open-hearth furnace or to a Bessemer converter where it is converted into steel.

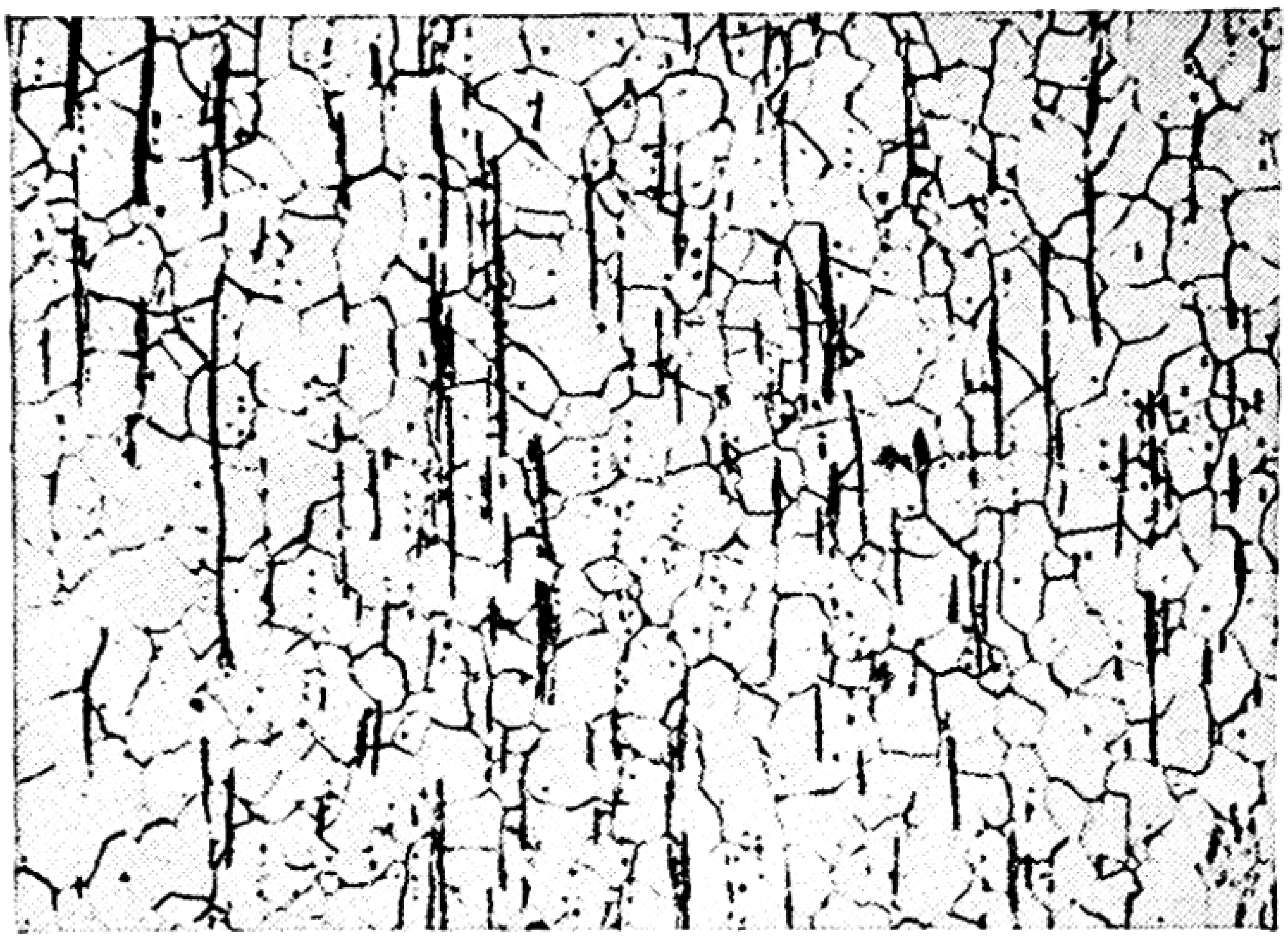

Fig. 3. Microscopic structure of wrought iron, longitudinal section (× 100). The black areas indicate slag. (*A. M. Byers Company.*)

4. **Wrought Iron.** The purest form of commercial iron, containing only about 0.1 per cent carbon and about 1 per cent slag, is known as *wrought iron.* Melted cast iron, mixed with iron oxide in the form of ore or rusty scrap iron, is placed in a *puddling furnace* with an arched roof of refractory brick to reflect the flames from the hearth. The oxide in the charge oxidizes the carbon, phosphorus, silicon, and manganese. The carbon dioxide escapes, and the oxides of phosphorus, silicon, and manganese form a slag. A pasty mixture of iron and slag formed during the stirring or puddling process is removed in large masses, or blooms, and worked to remove most of the slag. The presence of thin layers of slag in the iron contributes the properties of toughness and tensile strength to the iron. The production of wrought iron in the puddling furnace requires much labor and skill.

A more efficient method, known as the Aston process, was developed in 1925 by James Aston for the A. M. Byers Company of Pittsburgh. In this process, a specially refined iron in the molten state is poured into a specially prepared molten slag. The iron, which absorbs some slag, is compressed into blooms and then rolled into bars or billets.

In consequence of the high degree of toughness, tensile strength, malleability, and resistance to corrosion possessed by wrought iron, it is used for making pipe and tubing, chains, cables, and malleable-iron grillwork.

5. Steel. Cast iron and wrought iron do not have sufficient hardness and tensile strength (see Table I) to permit their use in the manufacture of machinery, tools, railroad rails, and bridges. The properties of iron and steel depend upon the percentages of carbon, silicon, manganese, phosphorus, and sulfur present, as well as upon the heat-treatment. The conversion of cast iron to steel consists mainly in reducing or removing the carbon, silicon, and other impurities in the iron by oxidation and slag formation.

TABLE I

COMPOSITION AND PROPERTIES OF IRON AND STEEL

	Pig iron (cast iron)	Wrought iron	Ordinary steel
Carbon, %	2 to 4.5	Less than 0.2	0.1 to 0.5
Other elements present	Si, Mn, S, P	$FeSiO_3$, slag	Mn (Si, S, P, in minute amounts)
Properties	Brittle, hard; low tensile strength	Malleable, tough, fibrous, relatively soft; intermediate tensile strength	Properties will vary with C content and heat-treatment; generally high tensile strength

Over 75 per cent of the cast iron or pig iron produced in the blast furnace is converted into steel. We shall now consider briefly the main processes for the manufacture of steel.

6. Bessemer Process. This process is named after Sir Henry Bessemer, who introduced it in 1855. The Bessemer *converter* is an egg-shaped vessel mounted on bearings so that it can be tipped for pouring the molten steel (Fig. 4). A 15-ton converter is about 12 ft. in diameter and 20 ft. high. Its lining usually consists of a siliceous (acidic) material and, in general, low phosphorus iron is used, hence the name *acid Bessemer process*.

Cast iron from the blast furnace, and still in the liquid state, is poured into the Bessemer converter. Compressed air is conducted through the hollow side mounting (trunnion) into the base (wind box) of the converter and blown up through tuyeres into the molten cast iron to oxidize the carbon, silicon, and other impurities to the corresponding oxides. The blowing operation requires only 10 to 15 minutes. When the air is first turned on, a shower of sparks followed by a brown smoke is produced as the manganese and silicon are oxidized. After about 5 minutes, the brown smoke is replaced by a brilliant flame sometimes 30 ft. in height, which is produced by the oxidation of the carbon. The order in which the oxidation of the elements proceed is determined by the amount of heat liberated during their oxidation. (For example, the heat produced in formation of 1 gram mole of oxide is greater for SiO_2 than for CO.) The control of the process depends upon the size and the color of the flame. Complete oxidation of the carbon is indicated by the sudden drop of the brilliant flame. Further blowing would oxidize a considerable amount of iron.

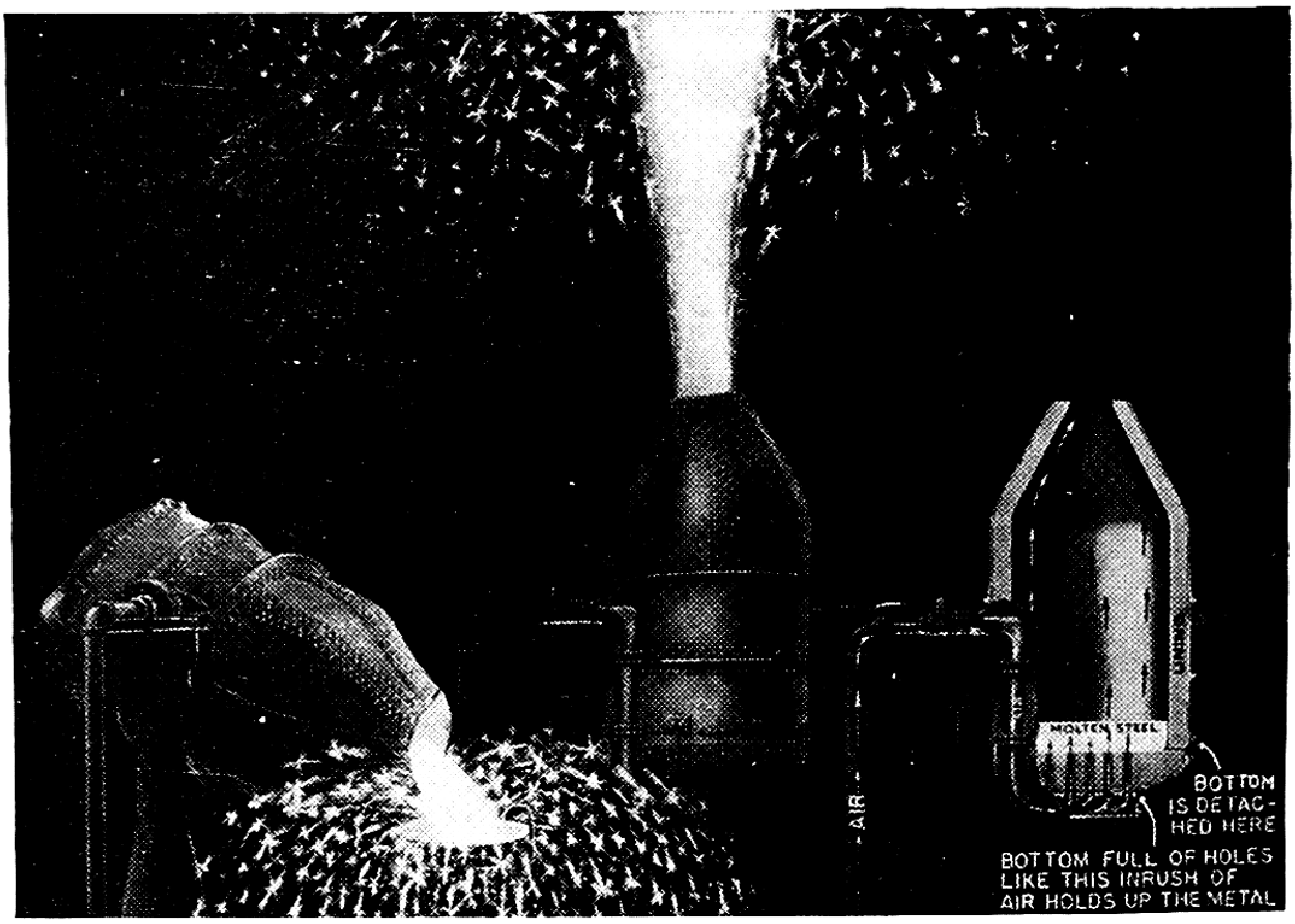
AIR
MOLTEN STEEL
BOTTOM IS DETACHED HERE
BOTTOM FULL OF HOLES LIKE THIS INRUSH OF AIR HOLDS UP THE METAL

FIG. 4. The Bessemer converter. (*United States Steel Corporation.*)

The manganese, silicon, and phosphorus are oxidized first, and then the carbon and sulfur. The air blast is stopped as soon as the carbon is oxidized and before much iron is oxidized. The gaseous oxides escape, and the solid oxides combine with one another or with an oxide from the lining of the converter to form an easily fusible slag which floats on the surface of the molten iron so that it may be removed separately.

Exercises

7. Write balanced equations for the formation of SiO_2, MnO, P_2O_5, CO_2, SO_2 by the reaction of oxygen with the corresponding elements in the Bessemer converter.

8. Write balanced equations for the formation of ferrous silicate, manganous silicate, calcium silicate, tricalcium phosphate, from the corresponding oxides, as occurs in the Bessemer process.

If the amount of phosphorus is high, a *basic lining* (lime brick) is used, and the last two reactions of Exercise 8 are of major importance in the slag formation process. If phosphorus is low, an *acid lining* (silica brick) is used, the last two reactions are unimportant, and but little phosphorus is removed.

After oxidation and slag formation have removed impurities as far as possible, the charge is poured into a ladle. Calculated amounts of carbon and any other alloying elements are then added to obtain a steel of the desired composition. At the same time, a small amount of a *deoxidizer* or *scavenger*, such as metallic manganese, aluminum, or titanium, is added. These elements react with iron oxide or with nitrogen, oxygen, or carbon monoxide gases in the steel and thus prevent flaws and gas bubbles in the finished product.

$$Mn + FeO \rightarrow MnO + Fe$$
$$2Al + 3CO \rightarrow Al_2O_3 + 3C$$

The oxides thus formed pass into the slag, and the steel is then ready for casting into ingots.

7. Open-hearth Process. About 100 tons of steel can be made in one "heat" in the open-hearth furnace (Fig. 5). The time required is about 10 hours. The *hearth* is a shallow basin about 30 ft. long and about 2 ft. deep, which is lined with a basic material containing calcium and magnesium carbonate; hence the term *basic open-hearth process*. This type of lining makes it possible to handle iron higher in phosphorus than the iron used in the acid Bessemer process.

The fuel gas and air pass through separate heated chambers containing loosely laid firebrick, before entering the hearth. The intense heat from the burning gas is reflected downward into the charge by the low roof just above it. The hot gases pass from the hearth through a second chamber of loosely laid brick which is heated to a high temperature. The flow of gases is then reversed so that the first preheating unit, now cooled, can be heated again. This ingenious method of conserving fuel and maintaining a high temperature is known as the *Siemens-Martin regenerative system.*

The charge of an open-hearth furnace always includes a certain amount of ferric oxide (rusty scrap iron or hematite) in addition to cast iron. This serves as an oxidizing agent to convert carbon, silicon, etc., into oxides. The ferric oxide thus replaces the oxygen of the air blast of the Bessemer process in that it acts as the oxidizing agent for the impurities. Slag formation and scavenger action follow the same principles as described in connection with the Bessemer process.

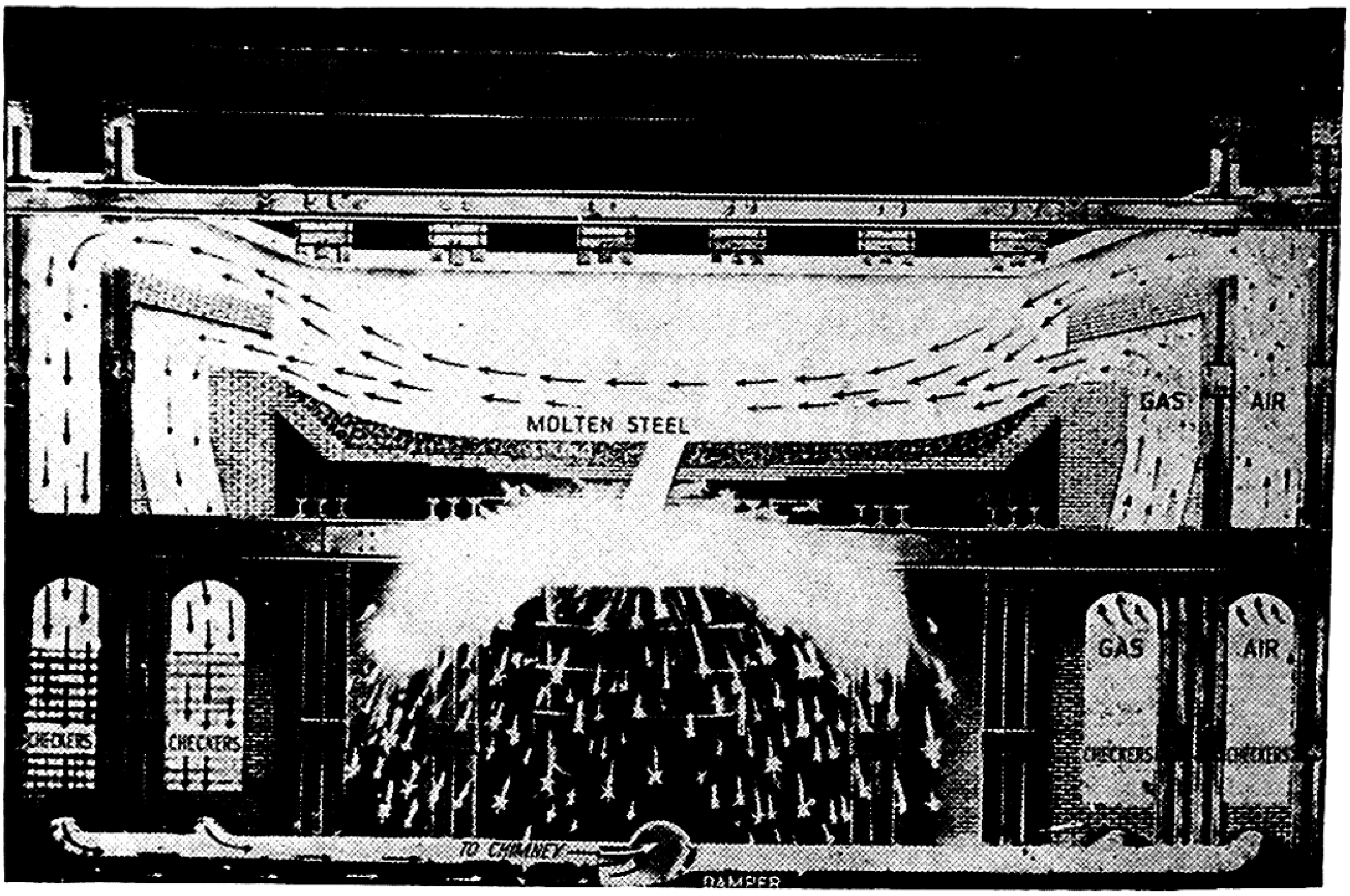

FIG. 5. The open-hearth furnace including the regenerative system. (*United States Steel Corporation.*)

More than three-fourths of American steel is now produced by the open-hearth process. Some of the advantages of the open-hearth process as compared with the Bessemer process are (1) more accurate control of the temperature and the composition of the metal and (2) use of scrap iron and iron from low-grade ores.

8. Electric Steel. An electric-arc or induction furnace (Fig. 6) allows closer control of temperature and other conditions, and such processes are often used for production of special alloy steels. The principles involved are identical with those described above: (1) oxidation of impurities in iron, (2) slag formation, (3) scavenger action, (4) addition of desired proportions of carbon and alloying elements.

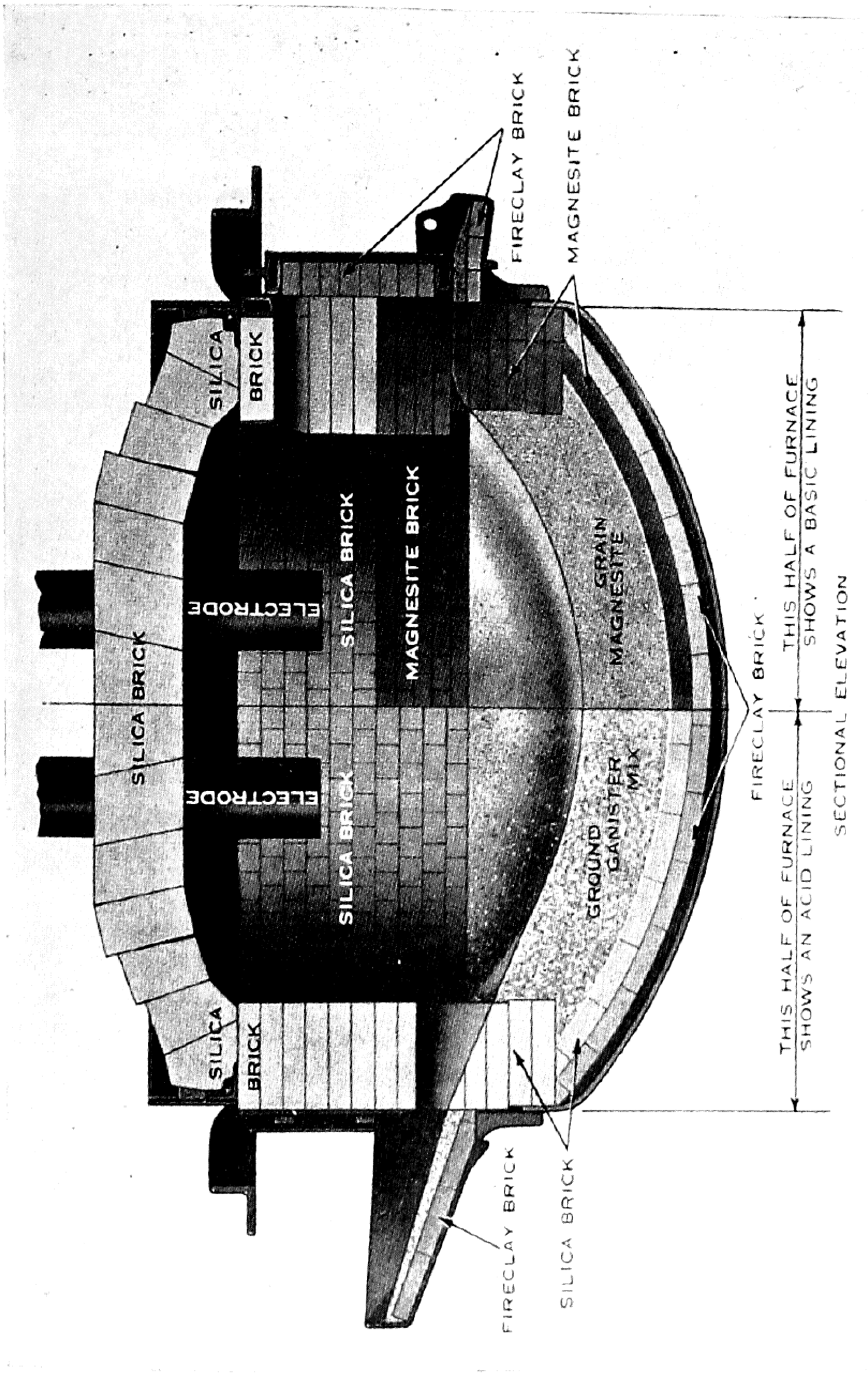

Fig. 6. Cross section of a Heroult electric-arc furnace for making steel. (*Harbison-Walker Refractories Company.*)

9. Alloy Steels. The addition of other metals to steel increases the tensile strength, hardness, and other important properties. These properties are very essential in steel used in the manufacture of axles, gears, and springs of automobiles, and other special uses. A number of alloy steels with some of their properties and uses are indicated briefly in Table II.

TABLE II
SOME ALLOY STEELS

Alloying elements	Properties	Uses
1. Chromium	Resists corrosion	Cutlery
2. Chromium-tungsten	Retains temper when red hot	High-speed tool steels
3. Chromium-vanadium	Resists wear and shock	Gears, axles
4. Manganese	Resists wear	Railway rails and rock crushers
5. Molybdenum	Resists heat and wear	Gears, axles, tools
6. Nickel	High tensile strength Resists corrosion	Bridge cables and trusses
7. Nickel-chromium	Very hard and tough	Armor plate
8. Vanadium	Resists shock and fatigue	Automobile springs

Exercises

9. What type of alloy steel would be needed for the construction of a high-pressure reaction chamber for the synthesis of ammonia?

10. What alloy of steel has been responsible for the development of the modern metal-machining industry?

10. Tempering of Steel. The hardness of steel can be controlled by the heat-treatment. Carbon forms a compound with iron, Fe_3C, known as *cementite*. When steel is cooled slowly, the cementite crystallizes as separate particles, and the steel is very soft. On the other hand, if the steel is cooled rapidly by immersing it in water or oil (*quenching*), the cementite exists in an unstable, supersaturated, solid solution, and the steel is very hard and brittle. Tempering is done by reheating quenched steel to give it the desired hardness. When the steel is reheated, it becomes softer and less brittle, owing to the partial separation of cementite.

11. Some Reactions of Iron and Its Ions. Iron, being above hydrogen in the activity series, reacts with hydrochloric and sulfuric acids, forming ferrous chloride and ferrous sulfate, respectively, and hydrogen.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Ferrous compounds are easily oxidized to ferric compounds by nitric acid and other oxidizing agents.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

Ferric thiocyanate, a deep-red compound, is formed from ferric ions and thiocyanate ions.

$$Fe^{+++} + 3CNS^- \rightarrow Fe(CNS)_3$$

Ferric ferrocyanide (*prussian blue*), used for laundry bluing, is formed from ferric ions and ferrocyanide ions.

$$4Fe^{+++} + 3Fe(CN)_6^{----} \rightarrow Fe_4[Fe(CN)_6]_3$$

The two reactions just described constitute very delicate tests for the presence of ferric ions in solution.

Ferrous ferricyanide (*Turnbull's blue*) is formed from ferrous ions and ferricyanide ions.

$$3Fe^{++} + 2Fe(CN)_6^{---} \rightarrow Fe_3[Fe(CN)_6]_2$$

This reaction is the basis of a well-known process for making *blueprints*.

12. Blueprinting. Sensitized paper containing ferric ammonium citrate and potassium ferricyanide is placed under a drawing on tracing paper and exposed to bright light. The ferric ions are reduced to ferrous ions by the effect of the light, and the ferrous ions react with the ferricyanide ions forming Turnbull's blue, $Fe_3[Fe(CN)_6]_2$, as indicated in the above equation. Under the black lines of the drawing, no ferrous ions are formed and no blue color (Turnbull's blue) is produced. When the paper is developed, the white lines of the drawing appear on a blue background.

SUGGESTED READING

———, Graphic Story of Steel, *J. Chem. Education*, **20**, 94 (1943).

Crook, Alloy Steels and Their Uses, *J. Chem. Education*, **4**, 583 (1927).

CHAPTER XXVIII

ALUMINUM, CHROMIUM, ZINC, MAGNESIUM

The metals aluminum and magnesium now have a very prominent status, particularly in the airplane industry, because of their lightness and tensile strength. Chromium is used in the manufacture of a great many alloys including stainless steel and tool steel. Its compounds are used extensively as pigments. The manufacture of brass and galvanized iron requires large quantities of zinc. The chemical properties of these metals and their compounds are quite diversified. In the qualitative analysis, however, use is made of certain common properties, *e.g.*, the amphoteric properties of aluminum, chromium, and zinc.

ALUMINUM

1. Occurrence. Aluminum is the most abundant metal in the earth's crust and is the third most abundant element. It is never found naturally in the free state. *Feldspar*, $KAlSi_3O_8$, and clay (impure kaolin, $HAlSiO_4$) are very abundant aluminum-bearing materials but are not used as a source of the metal because recovery is too expensive. *Bauxite* (impure $Al_2O_3 \cdot 2H_2O$) and *cryolite*, Na_3AlF_6, are the materials used in the process for obtaining metallic aluminum. Workable deposits of bauxite occur in Arkansas and Georgia, in Dutch Guiana, and in Russia. Cryolite is obtained from Greenland or by a synthetic process.

2. Production. The Hall-Heroult Process. Paul Heroult and Charles M. Hall, in 1886, independently discovered the modern electrolytic process for extracting aluminum from purified bauxite. It is interesting to note that both of these men were of the same age (twenty-two) and that both discovered the same process. The current price of aluminum is less than 20 cents per pound.

Bauxite is first purified to separate it from admixed iron oxide and other impurities, and the purified bauxite is then dissolved in molten cryolite. The resulting solution is electrolyzed, whereupon molten metallic aluminum is liberated at the cathode and collects at the bottom of the cell.

Oxygen is liberated at the carbon anodes where it forms carbon dioxide. As the Al_2O_3 is consumed in this process, fresh quantities of bauxite are added to the bath. The important parts of the diagram to be especially noted are the carbon lining of the cell which acts as cathode, the tap hole for removing aluminum, the carbon anodes, the composition of the electrolyte, and the materials liberated at each electrode.

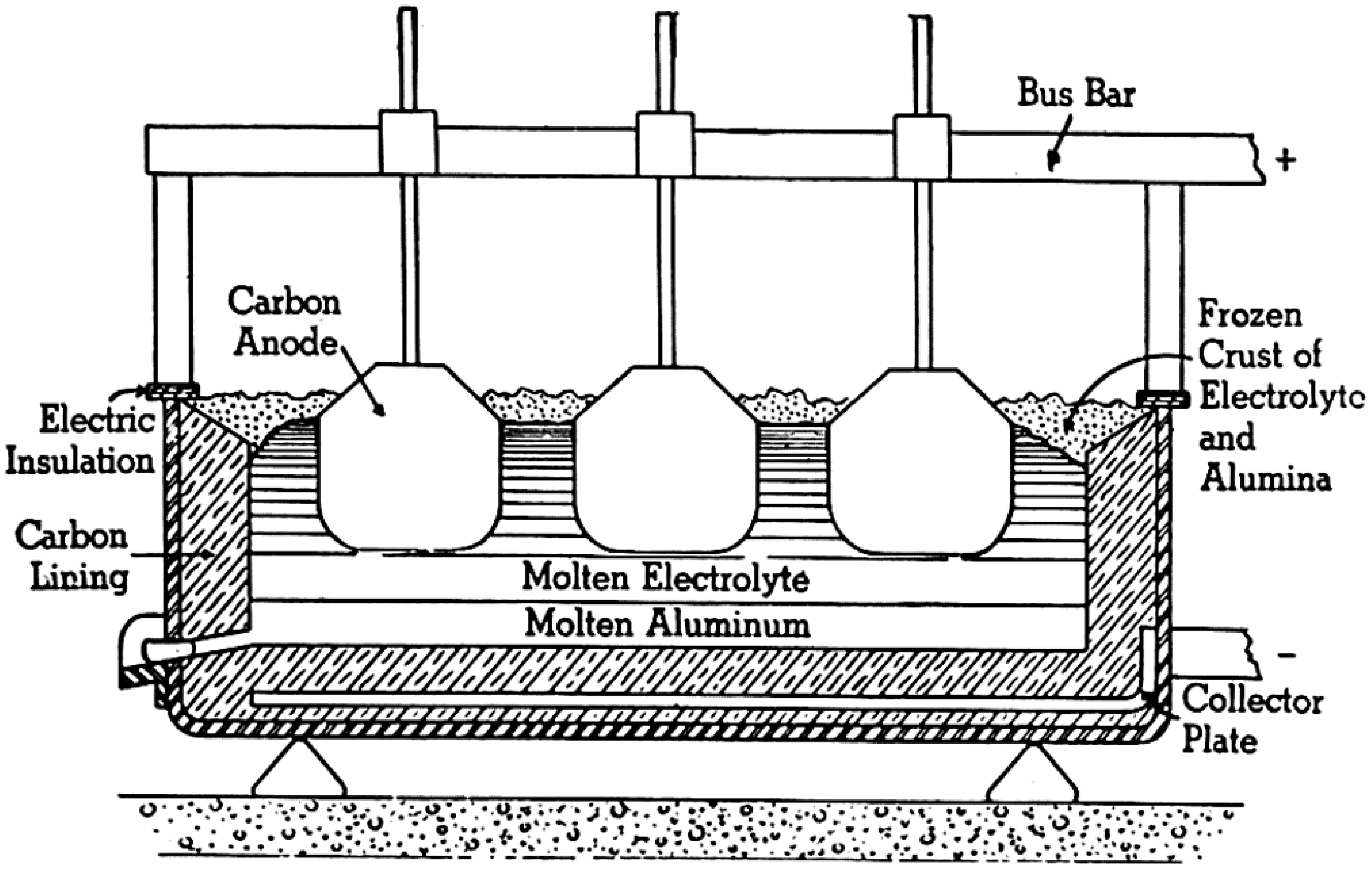

FIG. 1. Diagram of the electrolytic cell for production of aluminum. (*The Aluminum Company of America.*)

Exercise

1. Reproduce the labeled diagram of the electrolytic cell used for making aluminum.

3. Properties and Uses. The outstanding physical properties of aluminum are its low specific gravity (2.71) and its high tensile strength. It is ductile and malleable at ordinary temperatures. It is a better conductor of electricity than copper, on the basis of equal weights of the two metals.

The use of aluminum in cooking utensils is well known. Because of its lightness and strength, the metal is now used extensively in the construction of aircraft, automobiles, and railway cars. The mechanical properties of aluminum are much enhanced when alloyed with other metals. For this reason, the various alloys of aluminum are extensively employed in structural work.

4. Aluminum Alloys. The principal alloys are Dowmetal, duralumin, and magnalium (see Sec. 19). It is to be noted that the very low specific gravity of magnesium (1.74) makes the alloys that contain it much lighter than pure aluminum. Alloys of aluminum are harder and more easily machined than the pure metal.

5. Corrosion of Aluminum. Aluminum metal is quite resistant to the action of ordinary air and moisture because any exposed surface is quickly covered with an adherent layer of aluminum oxide. This layer is so thin as to be invisible, but it protects the metal underneath from further corrosion. This behavior is in marked contrast to the rusting of iron. Aluminum is readily corroded and dissolved by strong bases such as sodium hydroxide,

$$2Al + 2NaOH + 2H_2O \rightarrow \underset{\text{sodium metaaluminate}}{2NaAlO_2} + 3H_2$$

and by acids.

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$$

6. Thermite Process. When powdered aluminum and iron oxide are intimately mixed and then ignited by means of a burning magnesium ribbon or some flashlight powder, or other means, a violent reaction occurs.

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3 + \text{heat}$$

So much heat is liberated that the entire mass is heated to 3000°C., and the iron is heated far above its melting point. The process is used for certain special welding operations and for incendiary bombs. A related process utilizing Cr_2O_3 or MnO_2, instead of Fe_2O_3, is used to produce metallic chromium or manganese.

7. Alums. Potassium aluminum sulfate or *potash alum* has the formula, $KAl(SO_4)_2 \cdot 12H_2O$. This may also be written, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. All the alums are sulfates of a 1-valent and a 3-valent metal. Examples:

$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (soda alum)
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ (ammonium ferric alum)
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ (potash chrome alum)

Note that the last two compounds contain no aluminum but are nevertheless classed as alums. Alums are made by dissolving the proper sulfates in water in the proper proportions and then allowing evaporation and crystallization to occur. As alums crystallize readily, very large single crystals have been made. All the alums are *isomorphous; i.e.*, they have the same crystalline form. Alums have a multitude of uses, such as in water purification, dyeing, tanning, and in certain baking powders.

8. Aluminum Hydroxide. This compound may be made by addition of ammonium hydroxide to the solution of an aluminum salt.

$$\mathrm{Al^{+++} + 3OH^- \rightarrow Al(OH)_3}$$

It is a flocculent, gelatinous, almost colorless precipitate, useful in dyeing and in water purification. For the latter use, $\mathrm{Al(OH)_3}$ is usually made by the reaction of hydrated lime, $\mathrm{Ca(OH)_2}$, with alum or aluminum sulfate.

$$\mathrm{Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4}$$

For use in dyeing, aluminum hydroxide is usually made by hydrolysis of the aluminum salt of a weak acid. Hydrolysis is brought about by boiling,

$$\underset{\text{aluminum acetate}}{\mathrm{2Al(C_2H_3O_2)_3}} + \mathrm{6H_2O \rightarrow 2Al(OH)_3 + 6HC_2H_3O_2}$$

The formula $\mathrm{Al(OH)_3}$ is used only for convenience, since the composition of the precipitate does not correspond with this formula. The analysis of the precipitate varies with the conditions of formation and drying so that the true formula is probably $\mathrm{Al_2O_3 \cdot \mathit{x}H_2O}$. The term, *hydrous oxide*, is applied to such compounds; silica gel, $\mathrm{SiO_2 \cdot \mathit{x}H_2O}$, is another illustration.

9. Amphoteric Nature of Aluminum Hydroxide. An amphoteric hydroxide is one that will react either as an acid or as a base. Thus aluminum hydroxide may ionize in either of the following ways:

$$\mathrm{Al(OH)_3 \rightleftarrows Al^{+++} + 3OH^-} \qquad \text{(ionization as a base occurs in the presence of an acid)}$$

$$\mathrm{Al(OH)_3 \rightleftarrows H^+ +} \underset{\substack{\text{metaaluminate}\\ \text{ion}}}{\mathrm{AlO_2^-}} \mathrm{+ H_2O} \qquad \text{(ionization as an acid occurs in presence of a strong base)}$$

In more detail, the reaction of $\mathrm{Al(OH)_3}$ as a base may be illustrated thus,

$$\mathrm{Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O}$$

or

$$\begin{array}{rccl} \mathrm{Al(OH)_3} & \rightleftarrows & \mathrm{Al^{+++}} & + \mathrm{3OH^-} \\ \mathrm{3HCl} & \rightleftarrows & \mathrm{3Cl^-} & + \mathrm{3H^+} \\ & & \updownarrow & \quad \updownarrow \\ & & \mathrm{AlCl_3} & \mathrm{3H_2O} \end{array}$$

Reaction as an acid:

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

$$\begin{tikzcd}
Al(OH)_3 \arrow[r, shift left] & AlO_2^- \arrow[l, shift left] & + & H^+ & + H_2O \\
NaOH \arrow[r, shift left] & Na^+ \arrow[l, shift left] \arrow[d, shift left] & + & OH^- \arrow[d, shift left] \\
& NaAlO_2 \arrow[u, shift left] & & 2H_2O \arrow[u, shift left]
\end{tikzcd}$$

10. Aluminum Oxide and Aluminum Chloride. *Corundum* and *emery* are natural forms of aluminum oxide, Al_2O_3. Because of their hardness, these compounds are used as *abrasives*. A synthetic abrasive and refractory called *alundum* is made by fusing bauxite in the electric furnace.

Impurities in the native aluminum oxide impart beautiful colors forming the well-known and highly prized gems, *e.g.*, ruby (red), sapphire (blue). These gems are also made synthetically and are difficult to distinguish from the natural forms.

Anhydrous aluminum chloride, $AlCl_3$, is an important compound used in synthetic organic chemistry. Its use depends upon the fact that it forms numerous addition compounds. The preparation of certain dyes and a cracking process for making gasoline make use of aluminum chloride.

11. Portland Cement. This important building material is usually manufactured from clay and limestone, and small amounts of certain other materials must be present. In some regions these substances are found naturally in the proper proportions. The manufacturing operations consist in grinding and mixing, then heating strongly until partial fusion occurs, and finally, pulverizing to produce a gray powder. When made into a paste with water and with or without sand and/or other filler, this material will harden or set into a solid mass. This will occur as well under water as in air. The composition of portland cement may be expressed as CaO, Al_2O_3, SiO_2, although these oxides are combined to form various complex aluminates and silicates, *e.g.*, $3CaO{\cdot}Al_2O_3$, tricalcium aluminate and $3CaO{\cdot}SiO_2$, tricalcium silicate. The hardening or setting process involves the reaction of water with these compounds (hydration and hydrolysis).

Concrete is a mixture of cement, sand, and crushed stone or gravel, the proportions depending upon the purpose for which the concrete is to be used.

CHROMIUM

12. Occurrence and Metallurgy. Chromium is one of the less common metals and occurs mainly in the ore, *chromite*, $Fe(CrO_2)_2$. The United States is largely dependent upon foreign sources for this ore which is imported from Turkey, New Caledonia, the Philippines, India, and other countries.

Impure chromium known as *ferrochrome*, Fe and Cr, is obtained by reduction of chromite ore by carbon in the electric furnace.

$$Fe(CrO_2)_2 + 4C \rightarrow Fe + Cr + 4CO$$

Ferrochrome is used in the steel industry. Pure chromium may be obtained by reduction of chromic oxide, Cr_2O_3, by aluminum (Sec. 6).

$$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$$

Electrolytic chromium is deposited from an electrolyte of chromium sulfate, $Cr_2(SO_4)_3$, and other chromium compounds, *e.g.*, CrO_3, dissolved in water. The chromium-plated attachments of the modern automobile are familiar to every car owner. Chromium-plated steel has a bright and attractive appearance and is highly resistant to corrosion. The pure metal is hard and brittle and possesses a bright luster resembling silver.

13. Compounds of Chromium. The variable valence of chromium (+2, +3, +6) makes possible a considerable variety of compounds:

CrO	Chromous oxide	Black
Cr_2O_3	Chromic oxide	Green
CrO_3	Chromium trioxide	Red
K_2CrO_4	Potassium chromate	Yellow
$K_2Cr_2O_7$	Potassium dichromate	Orange

The lower valent compounds of chromium are reducing agents, and the higher valent compounds are oxidizing agents. The following equation is an illustration of the use of potassium dichromate as an oxidizing agent:

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

The oxidation of a 3-valent chromium compound is illustrated by the reaction of chromic chloride with sodium peroxide. The sodium peroxide is reduced.

$$\underset{\text{green}}{2CrCl_3} + 3Na_2O_2 + 4NaOH \rightarrow \underset{\text{yellow}}{2Na_2CrO_4} + 6NaCl + 2H_2O$$

This reaction is commonly used in the qualitative separation (Sec. 14) of aluminum and chromium ions.

14. Some Reactions of Aluminum and Chromium Ions. Both metals are commonly encountered in solution as 3-valent positive ions, Al^{+++} and Cr^{+++}, and can be precipitated by NH_4OH or $NaOH$.

$$Al^{+++} + 3OH^- \rightarrow Al(OH)_3\downarrow \quad \text{(white)}$$
$$Cr^{+++} + 3OH^- \rightarrow Cr(OH)_3\downarrow \quad \text{(green)}$$

The formulas $Al(OH)_3$ and $Cr(OH)_3$ are used for convenience only, since the corresponding compounds cannot be recovered from the precipitates. These precipitates are apparently hydrous oxides; *i.e.*, Al_2O_3 and Cr_2O_3 loosely combined with a variable and indefinite proportion of water which is gradually lost during any attempt to dry the precipitates. The precipitates are soluble in excess of a strong base such as NaOH.

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$
$$Cr(OH)_3 + NaOH \rightarrow \underset{\text{sodium meta-chromite}}{NaCrO_2} + 2H_2O$$

If an oxidizing agent such as Na_2O_2 or H_2O_2 is present during the above reaction, the $NaCrO_2$ is oxidized to Na_2CrO_4, but the $NaAlO_2$ remains unchanged.

$$2NaCrO_2 + 3H_2O_2 + 2NaOH \rightarrow 2Na_2CrO_4 + 4H_2O$$

When the resulting solution is acidified (after removing excess H_2O_2 or Na_2O_2), the $NaAlO_2$ is converted through $Al(OH)_3$ into Al^{+++}, but the CrO_4^{--} is converted to $Cr_2O_7^{--}$. Addition of NH_4OH to this solution precipitates $Al(OH)_3$ but not $Cr(OH)_3$. Chromate and dichromate can be changed, one into the other, by the addition of acid or base.

$$2CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{--} + H_2O$$
$$Cr_2O_7^{--} + 2OH^- \rightarrow 2CrO_4^{--} + H_2O \quad \text{(red to yellow)}$$

This color change is usually adequate to identify these ions, particularly if the green color of 3-valent chromium ion has been observed before oxidation. The yellow chromate ion can also be identified by the addition of lead ion which forms the yellow insoluble lead chromate, $PbCrO_4$, or *chrome yellow*, a well known pigment in the paint industry.

$$Pb^{++} + CrO_4^{--} \rightarrow \underset{\text{yellow}}{PbCrO_4\downarrow}$$

ZINC

15. Occurrence and Metallurgy. The most common zinc ore is *sphalerite* or zinc sulfide, ZnS. This ore is converted to zinc metal by oxidation to remove sulfur, followed by reduction with carbon.

$$\begin{array}{l}
2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \\
ZnO + C \rightarrow Zn + CO
\end{array}$$

Zinc metal is used for protective coatings on iron (*galvanized iron*), for making alloys (*brass*, Cu and Zn), and as one of the active materials in electric dry cells. Zinc oxide is commonly used in rubber compounding; zinc oxide, zinc sulfide are important white paint pigments.

16. Some Reactions of Zinc Ion. Zinc hydroxide, $Zn(OH)_2$, precipitated by hydroxyl ion is an amphoteric compound (Sec. 9). The reactions are illustrated by the following equations:

$$\underset{}{Zn^{++} + 2OH^-} \rightarrow \underset{\text{white}}{Zn(OH)_2\downarrow}$$

As a weak acid:

$$\begin{array}{lcccc}
Zn(OH)_2 & \rightleftharpoons & 2H^+ & + & ZnO_2^{--} \\
 & & & & \text{zincate} \\
 & & & & \text{ion} \\
2NaOH & \rightleftarrows & 2OH^- & + & 2Na^+ \\
 & & \updownarrows & & \downuparrows \\
 & & 2H_2O & & Na_2ZnO_2
\end{array}$$

As a weak base:

$$\begin{array}{lcccc}
Zn(OH)_2 & \rightleftharpoons & Zn^{++} & + & 2OH^- \\
2HCl & \rightleftarrows & 2Cl^- & + & 2H^+ \\
 & & \downuparrows & & \updownarrows \\
 & & ZnCl_2 & & 2H_2O
\end{array}$$

Ammonium hydroxide (NH_3) reacts with zinc ion, forming zinc ammonia complex ion. (Compare with similar reactions of silver and copper ions.)

$$Zn + 4NH_3 \rightarrow \underset{\text{colorless}}{Zn(NH_3)_4^{++}}$$

Hydrogen sulfide precipitates white zinc sulfide, ZnS, from basic, neutral, or slightly acid solutions.

$$Zn^{++} + S^{--} \rightarrow \underset{\text{white}}{ZnS\downarrow}$$

MAGNESIUM

17. Occurrence and Metallurgy. Sea water contains unlimited quantities of magnesium ion, Mg^{++}, and is an important source of the metal. Salt deposits usually contain magnesium chloride and other magnesium salts and, in the earlier development of the industry, salt brines were utilized. Magnesium is also found abundantly in natural deposits of *magnesite*, $MgCO_3$, and *dolomite*, $CaCO_3$ and $MgCO_3$, which resembles limestone.

In a plant operated by the Dow Chemical Company at Freeport, Tex., the first magnesium extracted from sea water was produced in January, 1941. The principal reactions in the process are illustrated by the following equations, using Mg^{++} from sea water, lime from clamshells, and hydrochloric acid.

$$Mg^{++} + \underset{\text{from lime}}{2OH^-} \rightarrow Mg(OH)_2\downarrow$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

$$\underset{\text{fused}}{MgCl_2} \xrightarrow{\text{electric current}} Mg + Cl_2$$

Exercises

2. Write equations to illustrate the formation of calcium hydroxide from clamshells, $CaCO_3$ (XXIX. 3 and 4).

3. Compare the electrolytic processes for producing magnesium and aluminum as to the materials used and the reactions involved.

Another process for the production of magnesium is based upon the reduction of magnesium oxide by carbon.

$$MgO + C \rightarrow Mg + CO$$

Exercise

4. Compare the reduction of magnesium oxide with the reduction of zinc oxide. What reaction would be used if magnesite were the source material for obtaining magnesium oxide?

It is interesting to note that, in 1915, only 87,500 lb. of magnesium was produced and sold for $5 per pound. In 1942 it was estimated that about 200,000,000 lb were produced. The selling price was about 20 cents a pound. The following is an excerpt from "Magnesium—A Magic Mineral" (pp. 43–45), by Lilian Holmes Strack, published by Harper & Brothers, in 1943:

> The advancement in the use of natural resources in the last hundred years is greater than that made in all of the previous years in history. Today, metals have come of age.
>
> Even though aluminum, iron, and magnesium are the most abundant com-

mon industrial metals in the earth's crust (not to mention the magnesium in the immeasurable waters of the sea), no one knew there was such a metal as magnesium until 1808. It was in 1825 that the first aluminum was taken from ore.

Most metals do much of their work in alloys. Rapid developments came when chemists took the two "new" light weight metals and alloyed them. They soon learned that by mixing certain quantities of each metal, and then giving the mixtures proper heat treatment and aging, they could get alloys which combine great strength with extreme lightness in weight.

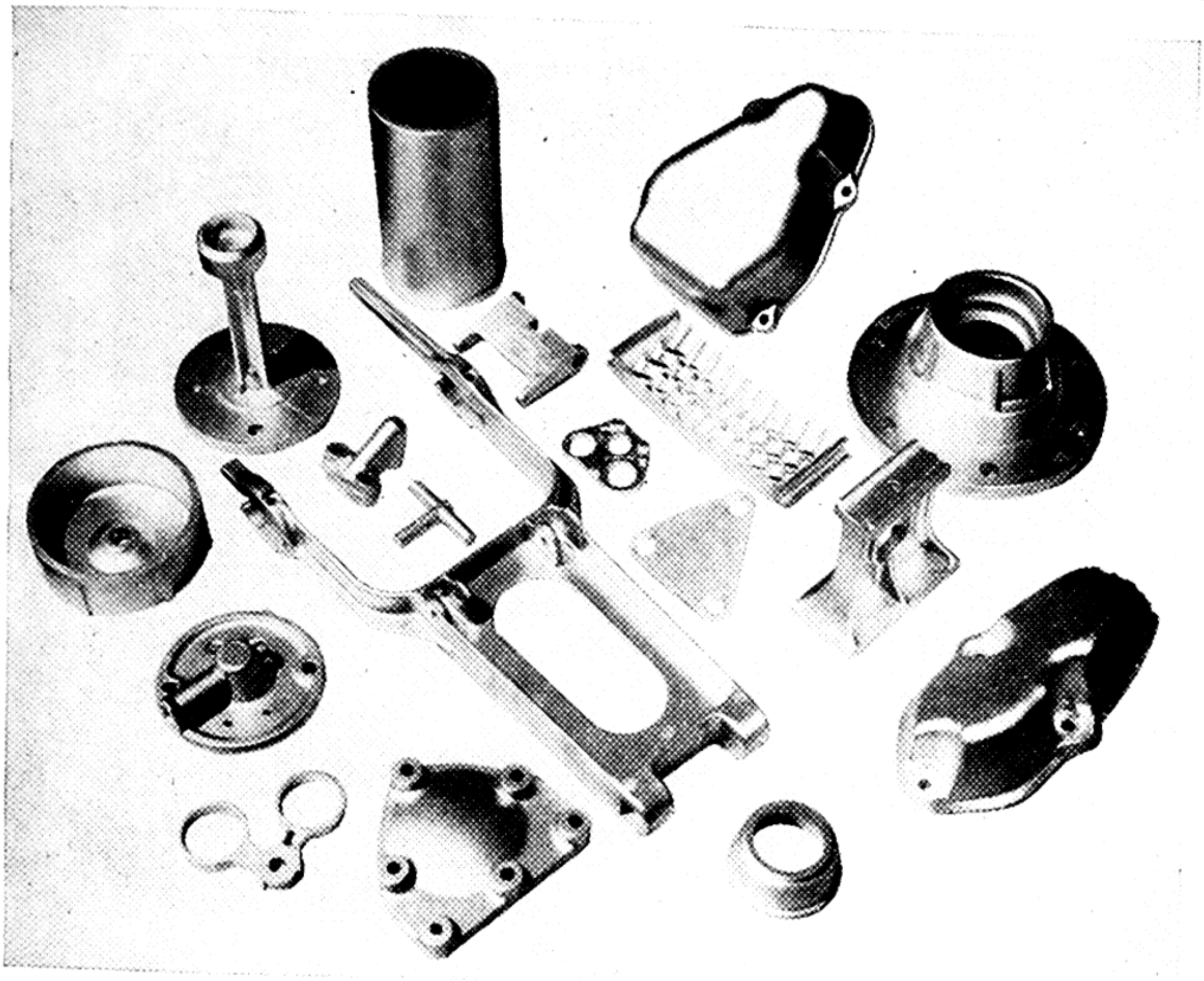

FIG. 2. Aircraft die castings of magnesium alloy. (*The Dow Chemical Company.*)

The old adage, "Birds of a feather flock together," holds good in the case of the almost feather weight metals, for each metal—just a bit of it—strengthens the other.

Naturally the lighter anything is, the less power it takes to lift or move it. Just so, the less power that is needed, the cheaper and easier the operation of the machinery, whether it be an automobile, a railway train, or fast-moving machine parts in a factory. That is why magnesium is making a place for itself and is used in many ways in various industries, such as electrical, chemical, aircraft, optical, rubber, and many others.

18. Properties of the Metal. Although magnesium is relatively high in the activity series, it does not readily undergo oxidation or corrosion unless it is in the finely divided state. In the powder form, however, it is readily ignited and emits a brilliant light, a property that makes it useful as flashlight powder. In welding magnesium parts, helium gas is used to exclude oxygen which would oxidize the magnesium at the high temperature (XVII. 8). The metal reacts rapidly with acids, forming the salt of magnesium and hydrogen. It is very easily machined.

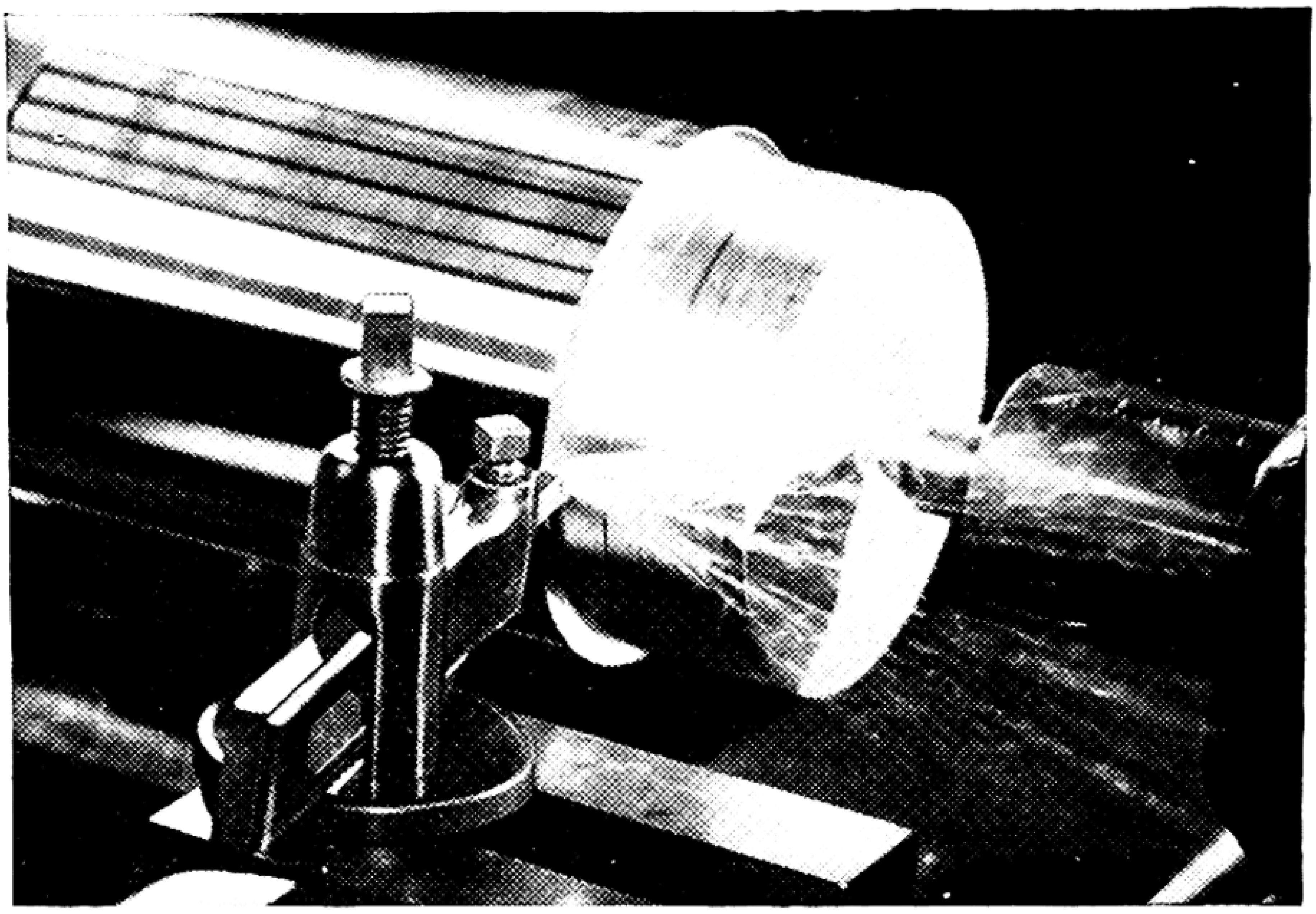

Fig. 3. Cutting magnesium on a lathe. Magnesium is the easiest of all metals to machine. Heavy feeds and depths of cut can be used at high speeds. (*The Dow Chemical Company.*)

19. Alloys of Magnesium. In the manufacture of the alloys of magnesium, the metals commonly used are aluminum, manganese, and zinc. Other metals, *e.g.*, copper and cadmium, are also used. In general, the hardness, strength, and durability of the alloys are greater than in the case of the pure magnesium. Among the well-known alloys are the following:

Dowmetal	Mg, Al, Mn, Zn
Duralumin	Mg, Al, Mn, Cu
Magnalium	Mg, Al, Cu

Some of the uses of the alloys of magnesium have already been mentioned in a previous connection (Sec. 17).

20. Some Compounds of Magnesium. A suspension of magnesium hydroxide, $Mg(OH)_2$, in water, known as *milk of magnesia* is often prescribed to neutralize excess acidity in the stomach. Magnesium sulfate, $MgSO_4 \cdot 7H_2O$, or *Epsom salts*, is another well-known pharmaceutical preparation used as a purgative.

A basic carbonate of magnesium, variable in composition, is mixed with 15 per cent *asbestos*, forming 85 *per cent magnesia*, an efficient and widely used insulating material for covering steam pipes.

Magnesium oxide, MgO, prepared by varying methods, finds wide application in toilet preparations, tooth pastes, special cements, insulators, and refractory materials.

NOTE: At this point the student should prepare a list of 10 or more exercises that summarize the processes, reactions, and compounds described in this chapter. Ability to write questions is just as important as the ability to answer questions.

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CHAPTER XXIX

CALCIUM COMPOUNDS, HARD WATER

Limestone, lime, marble, and gypsum are well-known building materials. Calcium is a constituent of these materials. The use and treatment of hard water is a chemical problem of great importance in industry and in the home.

1. The Alkaline Earth Family. Calcium is the most common member of the family. The other elements are strontium, Sr; barium, Ba; and radium, Ra. All these elements are so active that they are never found in the free state in nature. They react rapidly with cold water, oxidize rapidly in air or oxygen, and also unite with nitrogen to form nitrides. Their compounds are all quite similar. Radium is the only element of the group that undergoes spontaneous atomic disintegration.

2. Occurrence of Calcium. Calcium carbonate in the form of limestone is the most common nonsiliceous rock. Calcium carbonate also occurs as marble, calcite, pearls, shells, and coral. Calcium sulfate is also a common mineral. Its most common form is gypsum, $CaSO_4 \cdot 2H_2O$, but it also occurs as anhydrite, $CaSO_4$, and as alabaster. The latter is a variety of gypsum.

3. Manufacture of Lime by "Burning" Limestone. Heat causes the decomposition of limestone into lime or quicklime, CaO, and carbon dioxide gas.

$$CaCO_3 \rightleftarrows CaO + CO_2\uparrow$$

The term *burning*, as applied to this process, is a misnomer since there is no union of oxygen with either lime or limestone. The term arises from the burning of coal or other fuel to supply the heat required for the decomposition.

The older type of equipment for lime burning consisted of a vertical *kiln* into which a mixture of limestone and coal was placed, the coal being ignited and the draft controlled to carry out the operation. A newer type of equipment uses horizontal rotary kilns with limestone entering at one end and lime leaving, and hot combustion gases entering at the opposite end.

The decomposition of calcium carbonate is reversible so that CO_2 and CaO will reunite if left in contact, unless the temperature is very high. In order to lower the operating temperature, a good draft is maintained during the burning process. This removes CO_2 as rapidly as it is formed, so the reverse reaction is prevented, and the forward

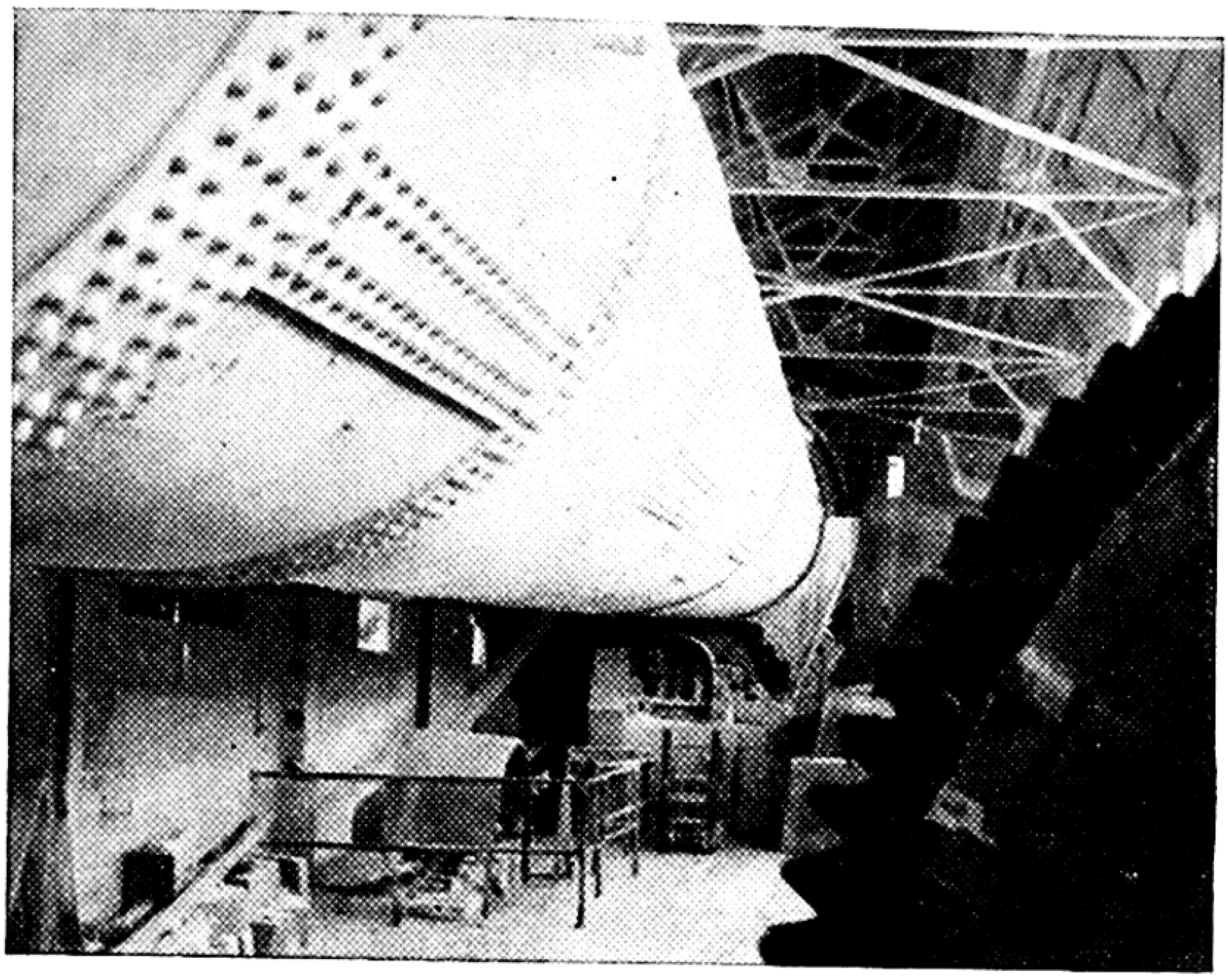

FIG. 1. A rotary lime kiln. (*The Warner Company, Bellefonte, Pa., plant.*)

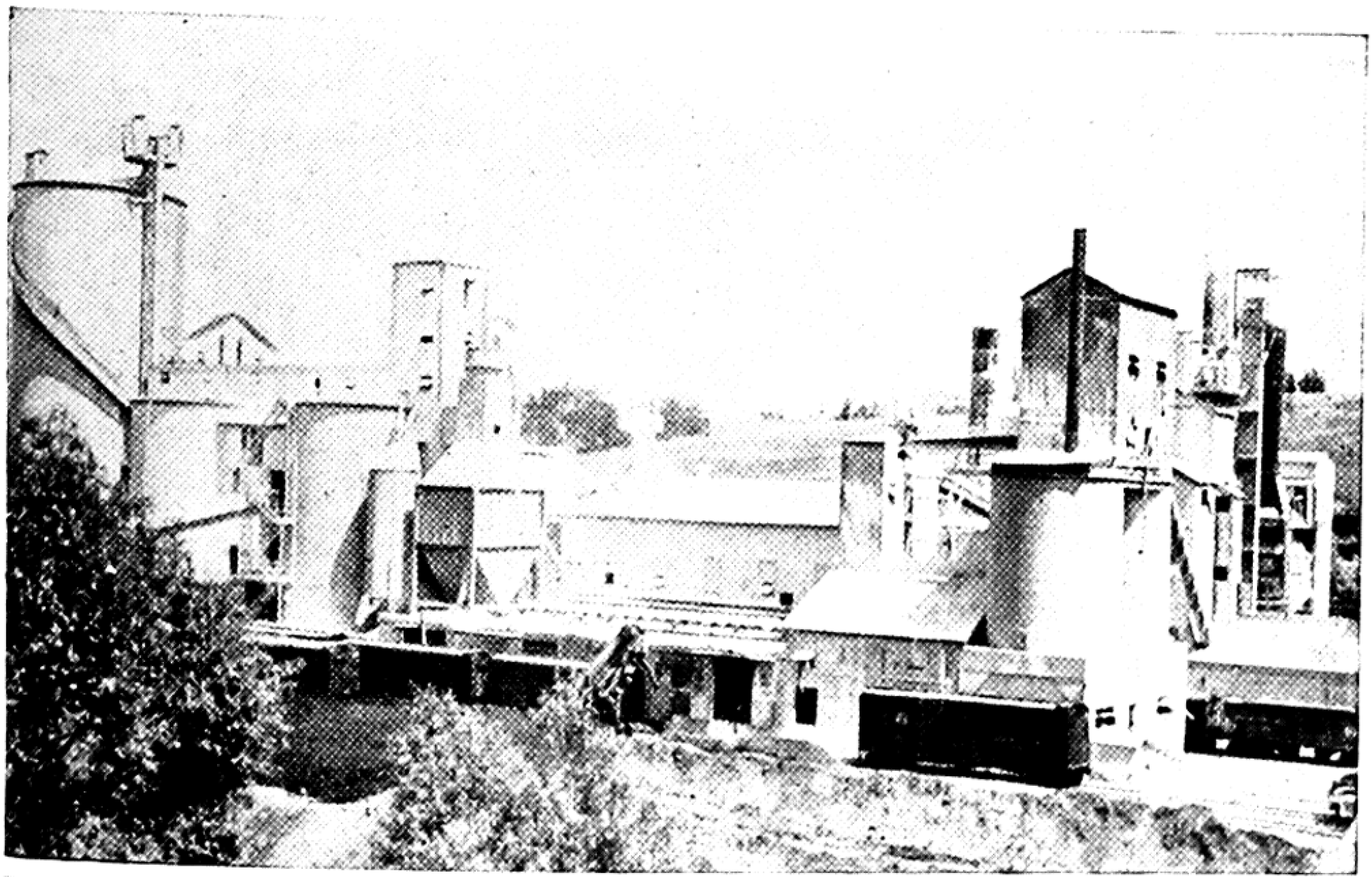

FIG. 2. A modern lime plant (the limestone is obtained from a mine). (*The Warner Company, Bellefonte, Pa., plant.*)

reaction is complete at a relatively low temperature. Too high a temperature not only increases the cost of fuel, but also causes fusion of impurities to form glasslike solids that interfere with the slaking of the lime.

Exercise

1. Calculate the weight of quicklime that can be made from 1 ton of limestone containing 95 per cent pure $CaCO_3$.

4. Slaking of Lime. Lime unites very readily with water to form calcium hydroxide. Much heat is liberated and the process is known as *slaking.*

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The product is known as *slaked lime* or *hydrated lime.* A solution or suspension of $Ca(OH)_2$ in water is known as *lime water* or *milk of lime,* widely used as an alkali in industry. On farms, it is used with copper sulfate in making bordeaux mixture for spraying potatoes, and as a whitewash on barns and fences. Application of lime to fields is a common procedure.

Exercise

2. Calculate the weight (*a*) of quicklime and (*b*) of water, required to make 1 ton of hydrated lime.

5. Air Slaking of Lime. If lime is allowed to stand in air, both of the following reactions occur:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$CaO + CO_2 \rightarrow CaCO_3$$

The product is known as *air-slaked lime.*

6. Lime Mortar. This material is made by making a paste of slaked lime, sand, and water. The sand is inert during the hardening process, but its presence prevents shrinkage and cracking upon hardening, and makes the mortar porous so that the carbon dioxide of the air may penetrate the mass. The hardening of mortar depends upon the union of carbon dioxide of the air with $Ca(OH)_2$ to form a mass of interlocking crystals of $CaCO_3$ that bind the entire mass into a solid.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Lime mortar will not harden under water. The plasticity of the wet mortar, the rate of hardening, and the final strength are altered by the presence of impurities, such as magnesium hydroxide, calcium aluminate, and calcium silicate, so that these materials must be kept at a minimum in lime that is to be used for mortar.

7. Plaster of Paris. $(CaSO_4)_2 \cdot H_2O$ is manufactured by careful heating of gypsum until it loses three-fourths of its water of crystallization.

$$\underset{\text{gypsum}}{2[CaSO_4 \cdot 2H_2O]} \underset{\text{hardening}}{\overset{\text{manufacture}}{\rightleftarrows}} \underset{\text{plaster of paris}}{(CaSO_4)_2 \cdot H_2O} + 3H_2O$$

When the white powder, $(CaSO_4)_2 \cdot H_2O$, is made into a paste with water, the above change is reversed and a mass of interlocked crystals of solid gypsum is formed in a comparatively short time.

If a temperature of 200°C., or higher, is used during the manufacturing process, a dead-burned plaster containing considerable anhydrous $CaSO_4$ is formed. Such plasters harden very slowly but finally become much harder and stronger than ordinary plaster of paris. The presence of added substances also retards the setting process.

Plaster of paris is used in making forms or casts for supporting broken bones. It is also used in large amounts for making borders and moldings in interior decorative work.

Exercise

3. Calculate (*a*) the weight percentage and (*b*) the mole percentage of water lost in converting gypsum to plaster of paris.

8. Hard Waters. The term *hard water* commonly refers to any water containing dissolved bicarbonates or sulfates of calcium, iron, manganese, or magnesium. *Temporary hardness* is that due to bicarbonates and may be removed by boiling the water. *Permanent hardness* is due to sulfates and is unaffected by boiling. Permanent hardness arises when ground waters flow through or over deposits containing gypsum or other mineral sulfates. Temporary hardness arises when waters containing carbonic acid flow through or over limestones or other carbonate deposits. Carbonic acid is usually present in ground water because carbon dioxide of the air dissolves and combines with the water.

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$

The carbonic acid converts limestone, normal calcium carbonate, $CaCO_3$, into acid calcium carbonate or calcium bicarbonate, $Ca(HCO_3)_2$ which is slightly soluble (XXI. 3). The equation is

$$H_2CO_3 + \underset{\text{insoluble}}{CaCO_3} \rightleftarrows \underset{\text{soluble}}{Ca(HCO_3)_2}$$

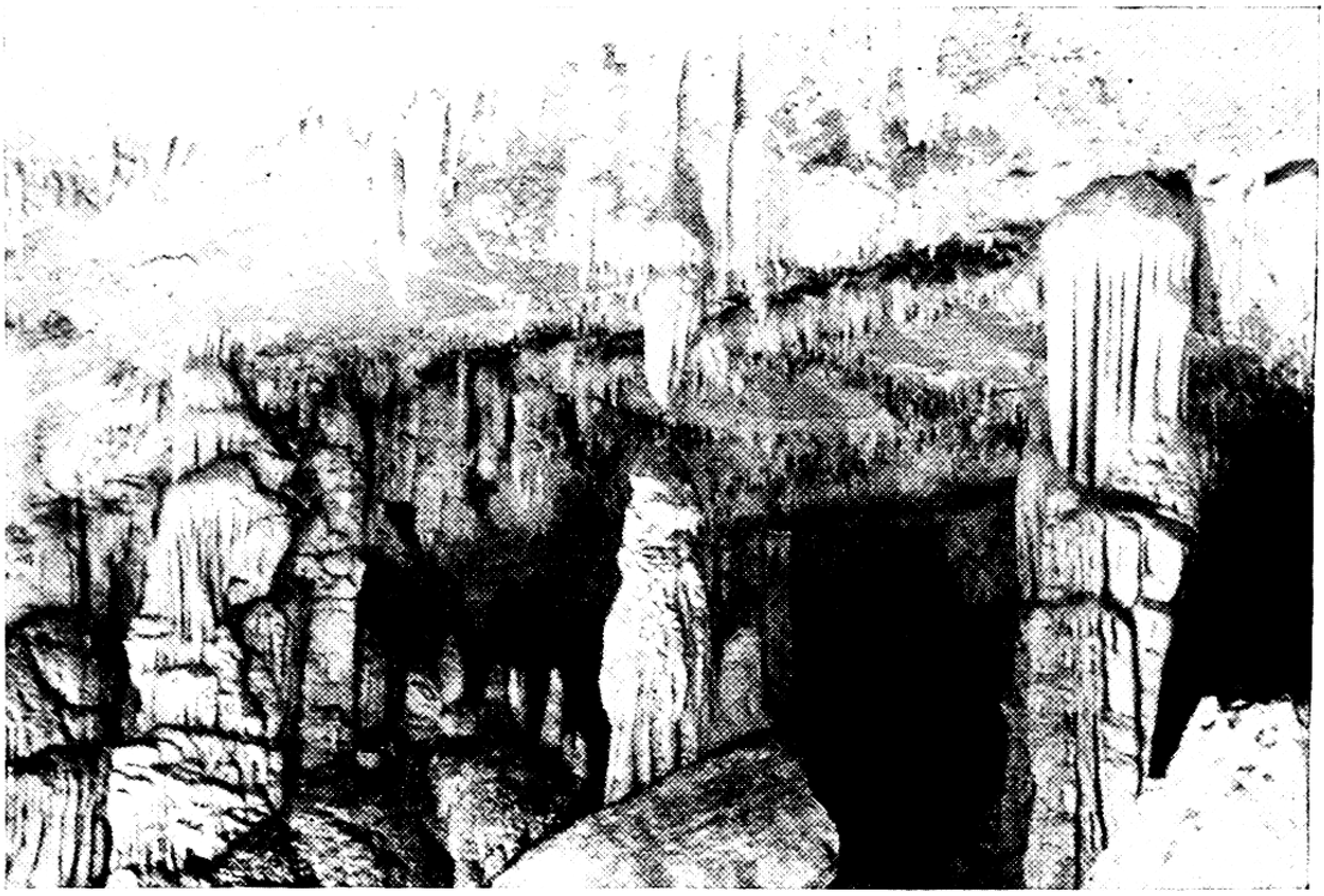

FIG. 3. Stalactites (*above*) and stalagmites (*below*) in a limestone cave. (*Courtesy of Penn's Cave, Centre Hall, Pa.*)

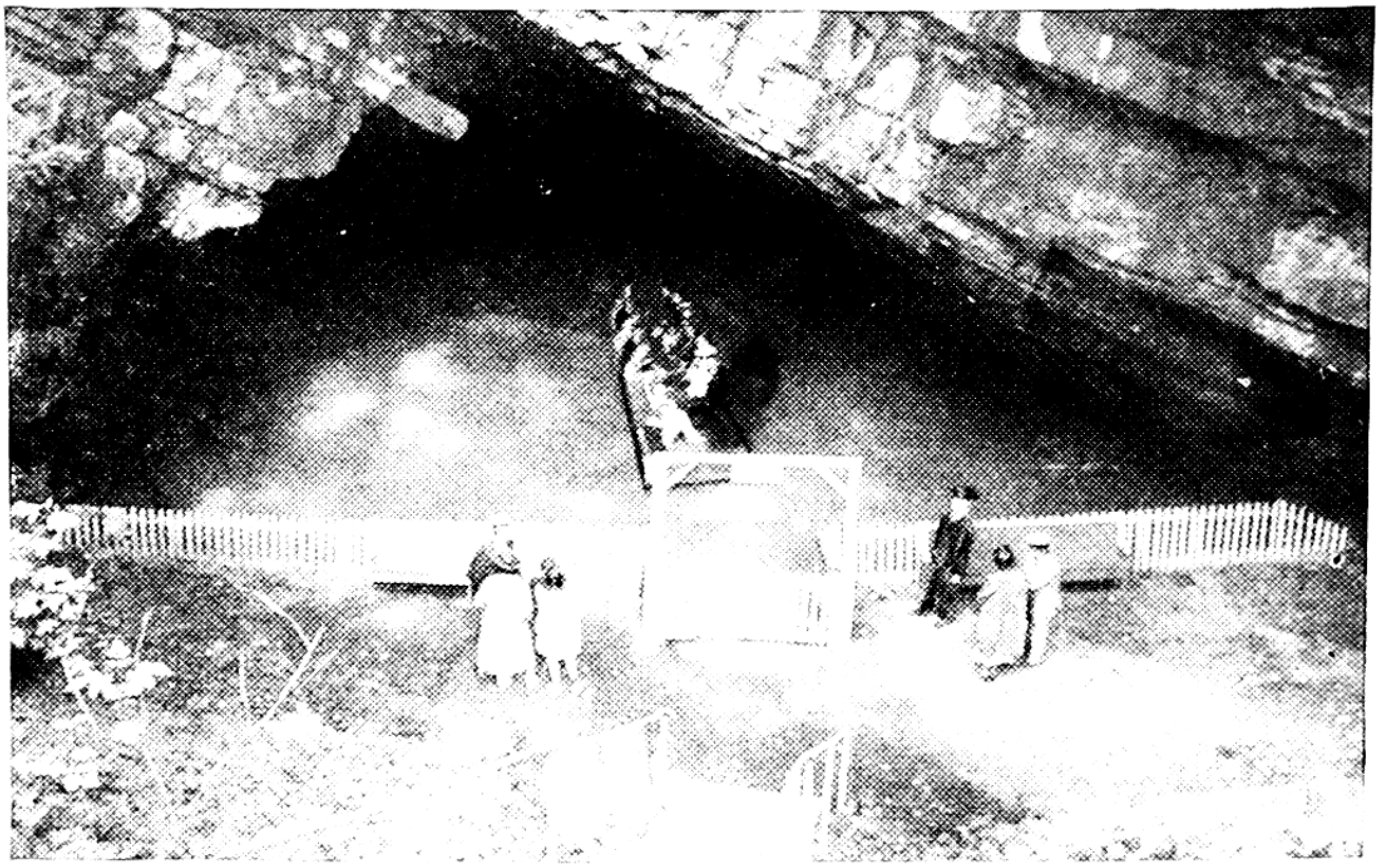

FIG. 4. Entrance to a limestone cave. (*Courtesy of Penn's Cave, Centre Hall, Pa.*)

This reaction not only accounts for the presence of temporary hardness in ground waters but also explains the formation of caves in limestone regions.

The reaction by which calcium bicarbonate is formed is reversible. Even a slight increase in temperature will decrease the amount of carbon dioxide dissolved in the water, and as a result the entire process is reversed and calcium carbonate is precipitated. By this process, *stalactites* and *stalagmites* are formed in caves. Obviously, the boiling of water containing calcium bicarbonate will cause complete reversal of the above reaction and removal of the temporary hardness.

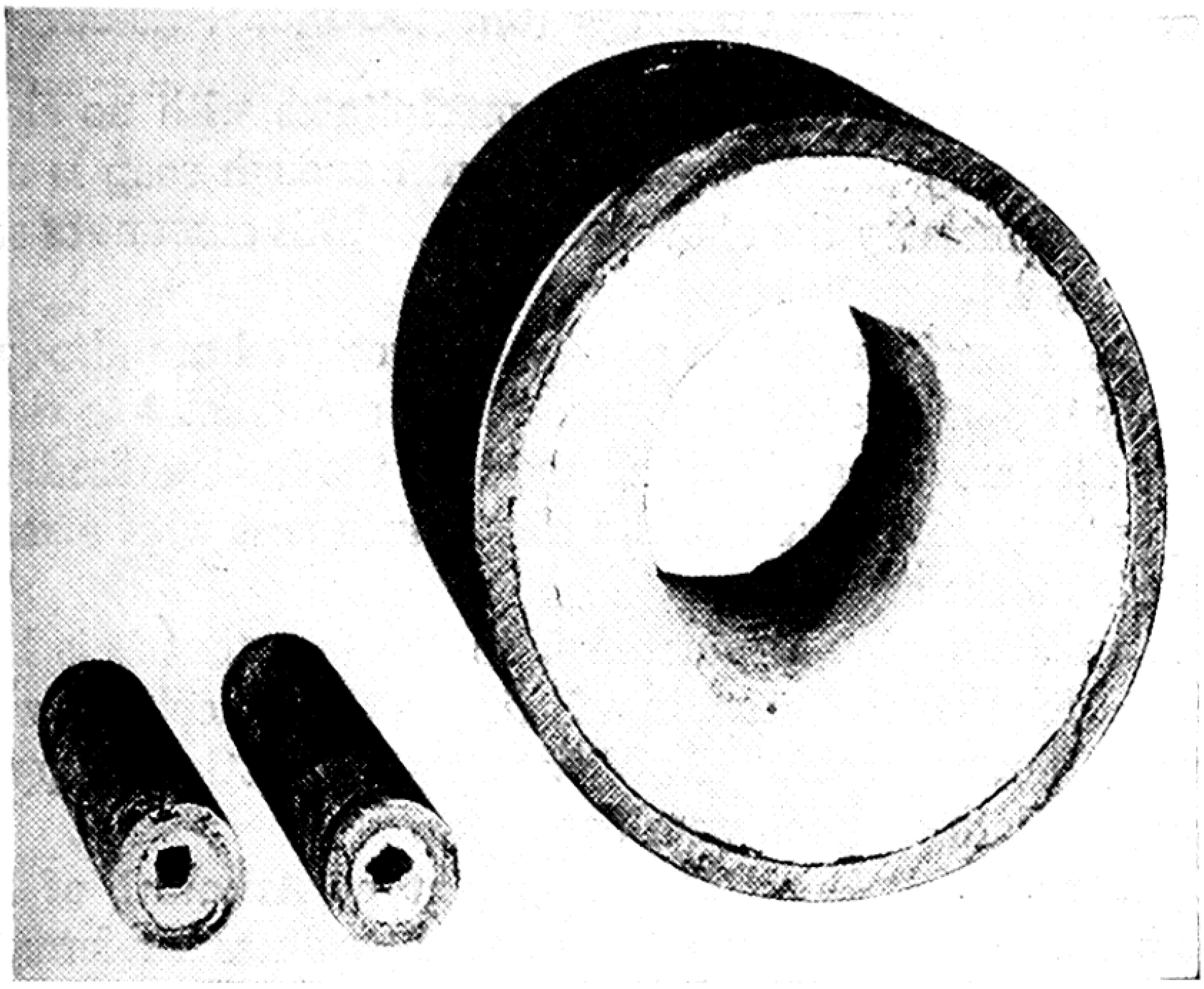

FIG. 5. Boiler-scale formation. (*The Permutit Company.*)

9. Consequences of the Use of Hard Water in Boilers. When water containing calcium bicarbonate is heated inside a boiler, the calcium carbonate is deposited there as a deposit or *scale*. Such a boiler scale is also formed when permanent hard water is evaporated in a boiler. In this case the scale is largely calcium sulfate, $CaSO_4$. Boiler scale decreases the rate of transfer of heat through the boiler wall and necessitates more heating with increased corrosion due to air and fuel gases on the outside of the boiler, and possible reaction of hot iron with steam. Consequently there is loss of efficiency and shortening of the life of the boiler. For this reason, most boiler water is *softened* before use, as explained below.

10. Waste of Soap by Use of Hard Water. Common soaps are a mixture of the sodium salts of complex fatty acids, such as sodium palmitate, $C_{15}H_{31}COONa$; sodium oleate, $C_{17}H_{33}COONa$; and sodium stearate, $C_{17}H_{35}COONa$ (XXIII. 10). These soaps react rapidly and completely with hard water according to the following equations:

$$\begin{aligned} Ca(HCO_3)_2 &+ 2C_{15}H_{31}COONa \rightarrow \overset{\text{calcium soaps}}{(C_{15}H_{31}COO)_2Ca} + 2NaHCO_3 \\ CaSO_4 &+ 2C_{17}H_{35}COONa \rightarrow (C_{17}H_{35}COO)_2Ca + Na_2SO_4 \end{aligned}$$

Since the calcium soaps are gummy precipitates with no cleansing power, no cleansing effect is obtained until enough soap is used to remove all hardness by the above reactions. This amount of soap is, therefore, wasted.

Iron soaps are formed in a similar manner, and are also gummy precipitates without cleansing power. They are difficult to wash out of clothes that are being laundered and have the further disadvantage that exposure to air converts them slowly into rust with a resulting brown stain on the clothes.

The term *hard water* originated from the fact that it is hard to wash in it. Sir Francis Bacon, in referring to the difficulty of washing with hard water, once said, "Chalky water is too fretting as appeareth in laundry of clothes, which wear out apace."

11. Water Softening. Measurement of Amount of Hardness in Water. Destruction or removal of hardness is referred to as *water softening*. The amount of hardness in any sample of water is measured in parts per million or in grains per gallon. This is determined by addition of a standard soap solution from a measuring tube (buret) until permanent suds are formed when the sample of water is shaken.

Exercises

4. (*a*) Calculate the weight in pounds of soap, $C_{17}H_{35}COONa$, that is used up by 2,000 l. water containing 200 g. $CaSO_4$ per 1,000 l. water (200 parts per million).

(*b*) One liter is about 1 qt. Calculate the number of gallons in 2,000 l. water.

5. (*a*) Calculate the weight in pounds of sodium carbonate required to precipitate the calcium ion as calcium carbonate from 2,000 l. water containing 200 g. $CaSO_4$ per 1,000 l. water (200 parts per million).

(*b*) Calculate the cost of the sodium carbonate used in (*a*), assuming a price of 6 cents per pound.

12. Lime Soda Method of Softening Hard Water. This method uses lime to remove temporary hardness and soda, Na_2CO_3, to remove permanent hardness.

$$\begin{aligned}&Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O\\ &CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4\end{aligned}$$

The amount of lime and soda added must be controlled so that there is but a small excess over that needed to remove the hardness. The precipitated $CaCO_3$ must be separated from the water by settling or filtration. The Na_2SO_4 remains in solution but does not react with soap, and does not form boiler scale.

Soda alone can be used for both temporary and permanent hardness since it reacts with $Ca(HCO_3)_2$ and precipitates $CaCO_3$. This is seldom done because Na_2CO_3 is much more expensive than lime. The reaction between $Ca(HCO_3)_2$ and Na_2CO_3 is indicated by the equation

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaHCO_3$$

Actually, the reaction is probably more complicated in that it involves hydrolysis of the Na_2CO_3 and interaction between the various ions present. Other sodium salts of weak acids that form insoluble calcium salts are also used as softeners. The most common examples are the following:

$$\begin{aligned}&2Na_3PO_4 + 3Ca(HCO_3)_2 \rightarrow Ca_3(PO_4)_3\downarrow + 6NaHCO_3\\ &Na_2SiO_3 + Ca(HCO_3)_2 \rightarrow CaSiO_3\downarrow + 2NaHCO_3\\ &Na_2B_4O_7 + Ca(HCO_3)_2 \rightarrow CaB_4O_7\downarrow + 2NaHCO_3\end{aligned}$$

13. Ion-exchange Processes for Water Softening and Purification. An established example of this is the *permutit process* in which the hard water that is to be softened is passed slowly through a tank filled with granules of a complex silicate known commercially as *permutit* (Fig. 6). Permutit belongs to a group of silicates known as *zeolites*. A simple zeolite would have the formula, $Na_2Al_2Si_2O_8$, and would react with calcium compounds as follows:

$$\begin{aligned}&CaSO_4 + Na_2Al_2Si_2O_8 \rightarrow CaAl_2Si_2O_8 + Na_2SO_4\\ &Ca(HCO_3)_2 + Na_2Al_2Si_2O_8 \rightarrow CaAl_2Si_2O_8 + 2NaHCO_3\end{aligned}$$

or, representing the zeolite ion by *Ze*,

$$Ca(HCO_3)_2 + Na_2Ze \rightarrow CaZe\downarrow + 2NaHCO_3$$

The silicates actually used are more complex in composition, but the effect is as indicated by these equations. The actual process involves migration of the sodium ions, Na^+, out of the crystal lattice of the silicate into the solution, and the migration of calcium ions, Ca^{++}, into the lattice to act as replacement.

It is obvious that, after a time, the sodium ions in the zeolite will be exhausted and the process must stop. Before this point is reached, the softening compound is regenerated by closing the connections to the water-supply lines, draining and filling with strong salt solution. The process is then reversed:

$$CaAl_2Si_2O_8 + 2NaCl \rightarrow Na_2Al_2Si_2O_8 + CaCl_2$$

so that calcium ions are removed from the zeolite lattice and sodium ions are recombined with it. The $CaCl_2$ and excess NaCl are washed out of the tank into the sewer, and the zeolite is again ready for service.

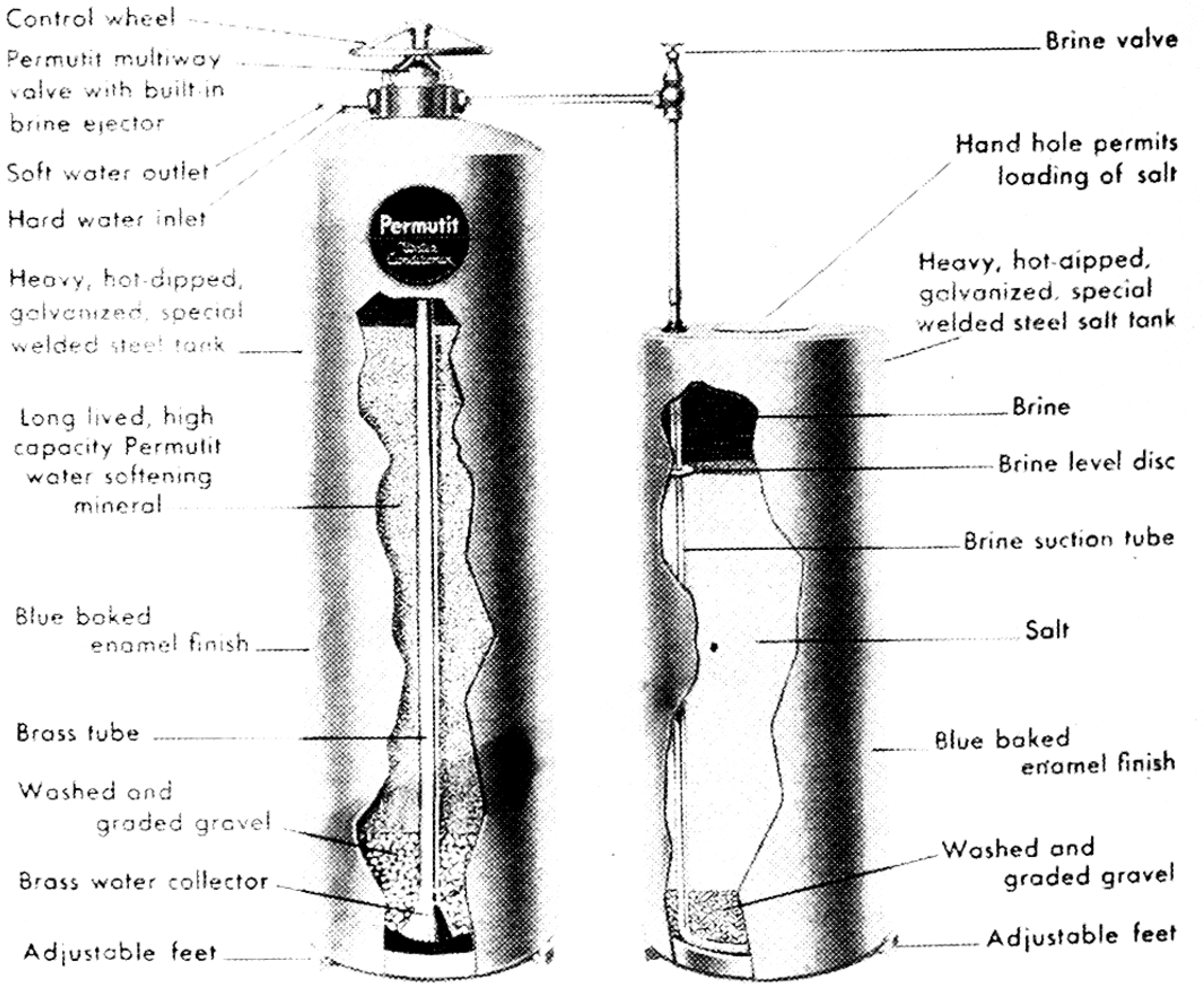

FIG. 6. Household water softener (Permutit process). (*The Permutit Company.*)

It has recently been discovered that certain synthetic resins also have ion-exchange properties and can serve to remove negative as well as positive ions from water. The product is known as *deionized* water. By the use of the zeolites and the ion-exchange resins, *water of zero hardness* or *zero water* can be obtained. The great majority of industries using water, *e.g.*, laundries, tanneries, vegetable processing and dairy plants, as well as heating and steam-power installations, use the zeolite or some other water-softening process. As a result, great operating economies and improvement in products are brought about. Many hospitals and homes also have water-softening equipment.

14. Some Reactions of Calcium Ions. From the analytical point of view, the principal reactions of calcium ions are the following:

$$\begin{aligned} Ca^{++} + CO_3^{--} &\rightarrow CaCO_3\downarrow \\ CaCO_3 + 2H^+ &\rightarrow Ca^{++} + H_2O + CO_2 \\ Ca^{++} + \underset{\text{oxalate ion}}{C_2O_4^{--}} &\rightarrow \underset{\text{calcium oxalate}}{CaC_2O_4\downarrow} \end{aligned}$$

The formation of the white crystalline calcium oxalate is a common test for the presence of calcium ions.

The so-called *flame test* is made by converting an insoluble calcium compound to the volatile calcium chloride by treatment with hydrochloric acid. By dipping a clean platinum wire into calcium chloride solution and then holding the wire in a clear blue flame, a bright deep-orange color is imparted to the flame. Barium compounds give a green color, and strontium compounds give a deep-red or crimson color, when tested in the same manner.

Sodium and potassium compounds may also be detected by the flame test. The sodium flame is yellow and the potassium flame is violet in color. Wires should, of course, be very carefully cleaned by being dipped in concentrated hydrochloric acid and heated strongly before a test is made.

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CHAPTER XXX

SODIUM AND POTASSIUM

Compounds of sodium and potassium are found naturally in great abundance and are of considerable industrial importance. The metals, lithium, sodium, potassium, rubidium, and cesium are placed in Group I of the periodic system. The hydroxides of these metals are all soluble in water and are strong bases or alkalies; hence the common name, *alkali metals*. In all their compounds, the elements of this group are monovalent.

1. The Metals. The properties of the free metals are closely related, as indicated in Table I. They react vigorously with water, liberating hydrogen, as we have learned. For example:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

or

$$Na + H_2O \rightarrow Na^+ + OH^- + \tfrac{1}{2}H_2$$

A general equation for the metals of the group is the following:

$$M + H_2O \rightarrow M^+ + OH^- + \tfrac{1}{2}H_2\uparrow$$

TABLE I

Element	Lithium	Sodium	Potassium	Rubidium	Cesium
Symbol	Li	Na	K	Rb	Cs
Atomic weight	6.9	22.9	39.1	85.4	132.9
Atomic number	3	11	19	37	55
Melting point, °C.	179	97.5	63.5	39.0	28.4
Density (20°C.)	0.53	0.97	0.86	1.53	1.9

Exercises

1. How do the melting points of the alkali metals vary with the atomic weights?
2. How do the densities of the alkali metals vary with the atomic weights?

2. Sodium. The metal sodium and the other metals of the alkali group, being very active elements, are never found naturally in the free state. Large quantities of sodium are used in the manufacture of sodium peroxide and sodium cyanide as well as numerous organic chemicals, including lead tetraethyl and synthetic indigo and other dyestuffs. The sodium vapor lamp is quite widely used in highway illumination where color discrimination is not required. The lamp emits an orange-yellow light, and its efficiency is estimated at about four times that of the ordinary tungsten lamp. It is said to be very economical in operation.

About 25,000 tons of sodium are produced annually by the electrolysis of fused sodium chloride.

3. Sodium Chloride, NaCl. The use of sodium chloride or common salt in preserving and cooking food, and in the preparation of freezing mixtures, is common knowledge. Industrially, it is the source material in the manufacture of caustic soda and chlorine, hydrochloric acid, and sodium carbonate.

Extensive deposits of sodium chloride are found in Michigan, New York, Ohio, Texas, in Germany and other countries. In some natural deposits, the layers are from 300 to 500 ft. or more in thickness, and the product is extracted by means of wells or by direct mining as in the case of coal. Sea water contains about 2.8 per cent of sodium chloride and is a direct source in areas where natural evaporation is utilized in separating the water, leaving the solid salt. Nearly 10 million tons of salt are used annually in the United States.

4. Sodium Hydroxide, NaOH. As stated in Chap. VIII, sodium hydroxide is made by the electrolysis of brine, a water solution of sodium chloride. It is a white, hygroscopic solid, very soluble in water, and is marketed in the form of sticks or flakes. It is one of the cheapest and most common alkalis and is used in a wide variety of industries, *e.g.*, in the refining of petroleum and the manufacture of soap.

5. Carbonates of Sodium. Solvay Process. There are two carbonates: (1) sodium bicarbonate, $NaHCO_3$, or *baking soda*, and (2) sodium carbonate, Na_2CO_3, or *soda ash*. The latter substance when fully hydrated forms $Na_2CO_3 \cdot 10H_2O$, or *washing soda*. These compounds are made from salt, ammonia, limestone, and water, by the Solvay process. Carbon dioxide, obtained by heating limestone, is passed into a solution of sodium chloride saturated with ammonia. The reactions are indicated by the following equations:

$$\mathrm{CaCO_3} \xrightarrow{\text{heat}} \mathrm{CaO} + \mathrm{CO_2} \tag{1}$$

$$\mathrm{NH_3} + \mathrm{H_2O} \longrightarrow \mathrm{NH_4OH}$$

$$\mathrm{NH_4OH} + \mathrm{CO_2} \longrightarrow \mathrm{NH_4HCO_3} \tag{2}$$

$$\mathrm{NH_4HCO_3} + \mathrm{NaCl} \longrightarrow \mathrm{NaHCO_3}\downarrow + \mathrm{NH_4Cl} \tag{3}$$

Sodium bicarbonate, which precipitates, is separated by filtration and is converted, by heat, into sodium carbonate or soda ash.

$$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2 \qquad (4)$$

The carbon dioxide formed in reaction (4) is used again in reaction (2).

Exercises

3. Write an equation to illustrate the recovery of ammonia from the ammonium chloride produced in reaction (3), using the calcium oxide from reaction (1).

4. Calculate (*a*) the number of pounds of Na_2CO_3 that could be made from 1 ton of $NaHCO_3$, (*b*) the number of pounds of $Na_2CO_3 \cdot 10H_2O$ that could be made from 1 ton of Na_2CO_3.

6. Baking Powders. Carbon dioxide in a dough makes it rise during the baking process, forming a light and porous bread or cake. Baking powders are added to the dough to produce the carbon dioxide. The ingredients of baking powders are (1) baking soda, $NaHCO_3$, (2) an acid salt or a salt that yields hydrogen ions by hydrolysis, and (3) cornstarch. The salts used may be potassium hydrogen tartrate (*cream of tartar*), $KHC_4H_4O_6$; primary sodium phosphate, NaH_2PO_4; primary calcium phosphate, $Ca(H_2PO_4)_2$; or anhydrous alum, $Na_2SO_4 \cdot Al_2(SO_4)_3$, the latter forming H^+ by hydrolysis. The reaction for the tartrate powder may be illustrated by the following equation:

$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow$$

The general reaction for any of the above types is as follows:

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2\uparrow$$

If baking soda alone is used in the baking, the carbon dioxide is liberated by the reaction of the bicarbonate with lactic acid in sour milk which is added to the dough. Heating also decomposes sodium bicarbonate, forming carbon dioxide and sodium carbonate.

Exercise

5. Write equations to indicate the formation of the H^+ (*a*) from $H_2PO_4^-$, (*b*) from the hydrolysis of $Al_2(SO_4)_3$.

7. Other Compounds of Sodium. Sodium nitrate or Chile saltpeter, $NaNO_3$, is an important raw material in the fertilizer industry. As the name indicates, it is obtained from natural deposits in Chile. Formerly an important source of nitric acid, it has been largely replaced by ammonia which is converted by catalytic oxidation to nitric acid (Ostwald process).

Sodium sulfate or *Glauber's salt*, $Na_2SO_4 \cdot 10H_2O$, *borax*, $Na_2B_4O_7 \cdot 10H_2O$, and sodium thiosulfate, or *hypo*, $Na_2S_2O_3 \cdot 5H_2O$, are compounds of industrial importance, the last being used in photography.

8. Potassium Compounds. Potassium chloride, KCl (*sylvite*), occurs abundantly in many salt deposits at Stassfurt in Germany and in Texas, New Mexico, and California. The fertilizer trade uses large quantities of potassium chloride, commonly known as *muriate of potash*. Potassium nitrate, KNO_3, has extensive application in the manufacture of gunpowder and fireworks and in the preservation of meats. It is made by the reaction of Chile saltpeter, $NaNO_3$, with potassium chloride. The potassium nitrate solution, when hot, is filtered off from the less soluble sodium chloride and then cooled, causing the solid KNO_3 to crystallize out of the solution. The equation for the reaction is as follows:

$$NaNO_3 + KCl \rightarrow NaCl\downarrow + KNO_3$$

The halides, KBr and KI, have medicinal uses and $KClO_3$, being a strong oxidizing material, is used in making fireworks. Potassium carbonate, K_2CO_3, is used in making certain types of glass. Potassium hydroxide, KOH, is used in the manufacture of liquid soap.

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APPENDIX

TABLE I
VALENCE NUMBERS (PARTIAL LIST)

1+	2+	3+	4+	5+	1−	2−	3−
H^+	Mg^{2+}	Al^{3+}	C^{4+} or 4^-	N (variable)	OH^-	O^{2-}	PO_4^{3-}
Na^+	Ca^{2+}	B^3	Si^{4+} or 4^-	P (variable)	Cl^-	CO_3^{2-}	AsO_4^{3-}
K^+	Ba^{2+}			As (variable)	Br^-	SO_3^{2-}	
Ag^+	Zn^{2+}				I^-	SO_4^{2-}	
Cu^+	Cu^{2+}				F^-		
NH_4^+					ClO_3^-		
Hg^+	Hg^{2+}				NO_3^-		
	Fe^{2+}						
	Sn^{2+}	Fe^{3+}	Sn^{4+}				
	Pb^{2+}		Pb^{4+}				

TABLE II
TEMPERATURE SCALES

	Fahrenheit	Centigrade	Absolute
Boiling point of water	212°	100°	373°
(at a pressure of 1 atm.)			
Freezing point of water	32°	0°	273°

Conversion of temperature readings from one scale to another:

Let F = Fahrenheit temperature,
C = centigrade temperature,
A = absolute temperature.

Then

$$F = \tfrac{9}{5}(C) + 32$$
$$C = \tfrac{5}{9}(F - 32)$$
$$A = \pm C + 273$$

TABLE III

VAPOR PRESSURES OF WATER (AQUEOUS TENSION)

Temperature, °C.	*Pressure, mm. of Mercury*
0	4.6
5	6.5
8	8.0
9	8.6
10	9.2
11	9.8
12	10.5
13	11.2
14	11.9
15	12.7
16	13.5
17	14.4
18	15.4
19	16.3
20	17.4
21	18.5
22	19.7
23	20.9
24	22.2
25	23.6
26	25.1
27	26.5
28	28.1
29	29.8
30	31.5
31	33.4
32	35.4
33	37.4
34	39.6
35	41.8
...	.....
100	760.0

TABLE IV

SOLUBILITIES OF BASES AND SALTS (AT 18°C.)*

(In grams per 100 ml. of water)

	K	Na	Ag	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.9	35.8	0.0_31†	37.2	51.0	73.1	55.8	203.9	1.4
Br	65.8	88.7	0.0_41	103.6	96.5	143.3	103.1	478.2	0.59
I	137.5	177.9	0.0_63	201.4	169.2	200.0	148.2	419.0	0.08
F	92.5	4.4	195.4	0.16	0.01	0.0_21	0.0_28	0.0_25	0.06
NO_3	30.3	83.9	213.4	8.7	66.2	121.8	74.3	117.8	51.6
ClO_3	6.6	97.1	12.2	35.4	174.9	179.3	126.4	183.9	150.6
OH	142.9	116.4	0.01	3.7	0.77	0.17	0.0_21	0.0_35	0.01
SO_4	11.1	16.8	0.55	0.0_32	0.01	0.20	35.4	53.1	0.0_24
CrO_4	63.1	61.2	0.0_22	0.0_33	0.12	0.40	73.0	.....	0.0_42
C_2O_4	30.2	3.3	0.0_23	0.0_28	0.0_24	0.0_35	0.03	0.0_36	0.0_31
CO_3	108.0	19.3	0.0_23	0.0_22	0.0_21	0.0_21	0.10	0.0_24?	0.0_31

* "Smith's College Chemistry," cover, D. Appleton-Century Company, Inc., New York, 1935.

† Small numbers are abbreviated, for example, $0.0_31 = 0.0001$.

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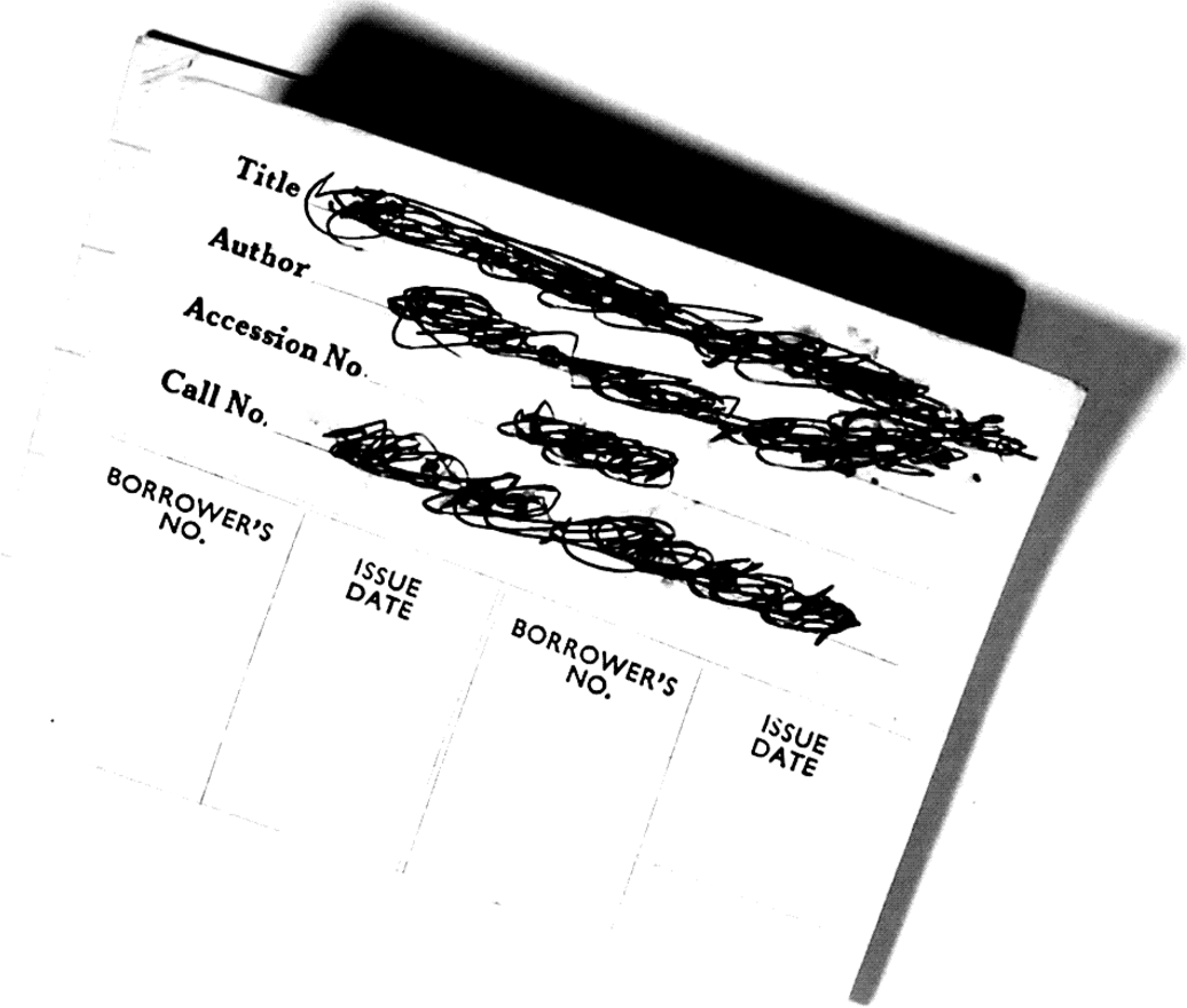

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TABLE II

PERIODIC CLASSIFICATION OF THE ELEMENTS (MENDELYEEV PLAN)

(Atomic numbers above symbols; atomic weights below symbols)

Series	Group 0	Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII		Group VIII		
	Inert gases	E_2O EH		EO EH_2		E_2O_3		EO_2 EH_4		E_2O_5 EH_3		EO_3 EH_2		E_2O_7 EH				
		A	B	A	B	A	B	A	B	A	B	A	B	A	B			
1		1 H 1.008																
2	2 He 4.003	3 Li 6.94		4 Be 9.02		5 B 10.82		6 C 12.01		7 N 14.008		8 O 16		9 F 19				
3	10 Ne 20.183	11 Na 22.97		12 Mg 24.32		13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.06		17 Cl 35.45				
	18 A 39.94	19 K 39.09		20 Ca 40.08		21 Sc 45.10		22 Ti 47.9		23 V 50.95		24 Cr 52.01		25 Mn 54.93		26 Fe 55.85	27 Co 58.94	28 Ni 58.69
			29 Cu 63.57		30 Zn 65.38		31 Ga 69.72		32 Ge 72.60		33 As 74.91		34 Se 78.96		35 Br 79.91			
		37 48		38 Sr 87.63		39 Y 88.92		40 Zr 91.22		41 Cb 92.91		42 Mo 95.95		43 Tc —		44 Ru 101.7	45 Rh 102.9	46 Pd 106.7
			47 88		48 Cd 112.41		49 In 114.76		50 Sn 118.7		51 Sb 121.76		52 Te 127.6		53 I 126.9			
				56 36		57 to 71 Rare earths		72 Hf 178.6		73 Ta 180.88		74 W 183.92		75 Re 186.31		76 Os 190.2	77 Ir 193.1	78 Pt 195.2
					80 .6		81 Tl 204.3		82 Pb 207.2		83 Bi 209.0		84 Po 210		85 At —			
						89		90 Th 232.1		91 Pa 231		92 U 238.07		93 Np —		94 Pu —	95 Am —	96 Cm —

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